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It was demonstrated that ionic liquids that are stable toward oxidation and nitration and are based on 1-n-butyl-3methylimidazloium cation (BMIm⁺) can be used as solvents and reaction media for copper dissolution in liquid dinitrogen tetraoxide N₂O₄. The ionic liquid not only favors dissociation of N₂O₄ into NO⁺ and NO₃⁻, but also takes part in the formation of different crystalline products. Thus NO[BF₄], NO[Cu(NO₃)₃] and (BMIm)₂[Cu₂(CF₃COO)₆] were prepared using (BMIm)A, A⁻ = [BF₄]⁻, (CF₃SO₂)₂N⁻, CF₃COO⁻, respectively. The formation of a certain product is determined by the nature of the anion A⁻ and the relative solubility of reaction products in the ionic liquid. Crystals of NO[BF₄] were also prepared directly from a mixture of N₂O₄ and BMImBF₄. According to the data of XRD single-crystal structure analysis, the structure of NO[BF₄] consists from tetrahedral [BF₄]⁻ anions and nitrosonium NO⁺ cations, the formation of these ions proving the heterolytic dissociation of N₂O₄ dissolved in the ionic liquid. The crystal structure of the earlier unknown binuclear copper trifluoroacetate (BMIm)₂[Cu₂(CF₃COO)₆] was also studied by XRD structure analysis. The peculiarity of this dimer compared to the majority of the known dimeric copper(II) carboxylates is the unusually long Cu--Cu distance (3.15Å), with Cu(II) ions demonstrating an atypical coordination of a distorted trigonal bipyramid formed by five O atoms of five trifluoroacetate groups.

Introduction

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Since early 1990s the interest to ionic liquids and to their unique properties is steadily growing. This can be explained by the variability of the reactivity of many chemical compounds being dissolved in ionic liquids. As a result, the synthesis of known products can be simplified in many cases, whereas new, previously unknown products can be synthesized in ionic liquids, including inorganic compounds.¹ In this concern, the use of ionic liquid as a reaction medium for the reactions between metals and liquid dinitrogen tetroxide (N_2O_4) is of special interest.

Dissolution of metals in liquid N_2O_4 serves as a general method of synthesis of nitrosonium nitratometallates $NO_m[M(NO_3)_{n+m}]$.² This method was developed in 1950s and the main reaction can be presented as:

 $M + (n+m)N_2O_4 \rightarrow NO_m[M(NO_3)_{n+m}] + nNO^{\uparrow}$

In most cases, the reaction requires the addition of a polar N- or Ocontaining organic solvent to liquid N_2O_4 , which results in an increase of the extent of heterolytic dissociation of dinitrogen tetraoxide with

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the formation of nitrosonium cations. The latter serve as an oxidant acting to transform a metal into the dissolved state:

 $N_2O_4 + Solv = NO^+_{solv} + NO_3^-_{solv}$ M + n NO⁺ \rightarrow Mⁿ⁺ + n NO

Nitrosonium nitratometallate can be precipitated from this solution by adding an excess of N_2O_4 , whereas in the case of an insufficient amount of N_2O_4 , solvent molecules enter the coordination sphere of the complexing metal atom.²

Taking into account the polar nature of ionic liquids, we assumed that they will facilitate the dissociation of N_2O_4 and will cause the dissolution of metals. In such a case, not only nitrates, but also some other products containing a cation and/or an anion of the ionic liquid can be obtained. Noteworthy that non-aqueous solutions containing cations of d- and f-elements can find application as catalysts in organic synthesis.³ The objective of this work was to check the above assumption on the use of ionic liquids as reaction media for the reactions of metals with liquid N_2O_4 by taking copper as an example of the metal. The ionic liquids that are rather stable toward oxidation and nitration were chosen, namely, those based on 1-n-butyl-3methylimidazolium cation (BMIm)A with the following anions A⁻⁼ [BF₄]⁻, (CF₃SO₂)₂N⁻, and CF₃COO⁻.

Results and discussion

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Interaction of ionic liquids with liquid N_2O_4 , synthesis and crystal structure of $NO[BF_4]$

The first stage of the study was focused on the elaboration of the effect of the ratio between the ionic liquid (*IL*) and dinitrogen tetraoxide. A mixture of equal volumes of liquid N_2O_4 and *IL* under some cooling (to 5-10°C) was stirred in sealed ampules and was left at room temperature for one week. In the case of BMIm[BF₄] as *IL*, tiny crystals precipitated from a pale-brown solution almost immediately after mixing the components. When the tiny crystals were kept for 45 days at 40°C, the average size of the crystals increased, so that single-crystal XRD structure analysis could be performed. This analysis showed that the precipitate represented nitrosonium tetrafluoroborate NO[BF₄] (I) (Table 1). When the starting mixture was cooled to 0°C, the yield of the precipitate increased noticeably.

Colorless crystals of I are prompt to fast decomposition in humid air due to the action of water vapors. The crystals are dissolved in water with evolution of gaseous nitrogen oxides, NO and NO₂, which is characteristic for nitrosonium salts.

In the case of dissolution of N₂O₄ in other ionic liquids BMImA used in this work, no precipitate formation was found. The experiments showed a rather high chemical stability of the BMIm⁺ cation with respect to the interaction with nitrogen (IV) dioxide, which is a strong oxidizing as well as nitrating agent. During the storage of the mixture of BMIm[BF₄] with N₂O₄ in a sealed ampoule at 40°C for 45 days, no noticeable changes and no formation of side products were observed.⁴

The structure analysis data for the products of the syntheses are presented in Table 1. The ionic structure of (NO)[BF₄] (I) includes nitrosonium cations and tetrafluoroborate anions, with the environment of a boron atom being a weakly distorted tetrahedron formed by four fluorine atoms (Fig. 1). Two B-F distances (1.385(1), 1.386(1) Å) are somewhat shorter than the two others (2×1.406(1) Å), and the F-B-F angles are varying between 108.43(9)° and 111.25(9)°.

The N-O bond length in a disordered NO⁺ cation is equal to 1.017(2) Å, which, according to the literature data, corresponds to a typical bond length in a nitrosonium cation.⁵ The positions of N and O atoms are linked by crystallographic mirror plane and are, therefore, indistinguishable. Each NO⁺ cation forms contacts with fluorine atoms of seven surrounding [BF₄] tetrahedra at distances N(O)…F ranging within 2.62–2.92 Å.

It should be noted that the structure I is isotypical of alkaline metal tetrafluoroborates $A[BF_4]$ (A=K, Rb, Cs).⁶ All these isostructural compounds, similar to I, are crystallized in an orthorhombic space group *Pnma* and adopt the same packing motif with the only difference that the diatomic NO⁺ cation is replaced for a monoatomic cation A^+ located on a mirror plane. The sizes of the unit cells increase with increasing size of the cation in the row K < NO < Rb < Cs.

Dissolution of N_2O_4 in the ionic liquid BMIm[BF₄] with the formation of crystals of I is the direct evidence that ionic liquids promote heterolytic dissociation of dinitrogen tetraoxide: BMIm[BF₄] + $N_2O_4 \rightarrow$ BMIm[NO₃] + NO[BF₄] The occurrence of this reaction is confirmed by the Kasults of XRD study of the precipitate formed. The X-Pay diffraction pattern of the polycrystalline sample demonstrates the good agreement with the theoretical diffraction pattern derived from the single-crystal structure data and also with XRD data for NO[BF₄] reported in ⁷. The presence of several peaks due to admixtures, with the overall intensity below 1-2% of the intensity of the main reflections, can be explained by the partial decomposition of the sample in the course of the X-ray experiment. The parameters of the unit cell of sample I somewhat increased compared to the parameters determined by X-ray structure analysis due to the difference in the temperatures of the measurements in X-ray structure analysis (150 K) and powder XRD (298 K) (see the Supplementary Information).

Table 1. Crystallographic data and some details of data collection and refinement

Formula		(BMIm) ₂	
	NO[BF4]	[Cu ₂ (CF ₃ COO) ₆]	
ICSD number	CSD 432338	CCDC 1520782	
Crystal system	orthorhombic	monoclinic	
Space group	Pnma	P21/n	
<i>a,</i> Å	8.856(2)	16.466(3)	
<i>b,</i> Å	5.6314(14)	15.871(3)	
<i>c,</i> Å	6.8410(16)	17.043(3)	
<i>α</i> , °	90.00	90.00	
<i>θ</i> , °	90.00	117.32(3)	
γ, °	90.00	90.00	
<i>V,</i> Å ³	341.17(14)	3957.1(14)	
Ζ	4	8	
d cal, g cm ⁻³	2.274	1.819	
λ (MoK _α), Å	0.71073	0.71073	
Crystal dimensions, mm	0.5×0.5×0.2	0.60×0.11×0.08	
Temperature, K	150(2)	100(2)	
<i>Ө</i> (max), °	28.48	29.18	
Reflections. number	458	10646	
unique			
Reflections. number with	417	6311	
F ² >2σ(F ²)			
Parameters in refinement	37	657	
wR ₂ (F ²)	0.054	0.077	
R ₁	0.021	0.042	
Goodness of fit	0.939	1.032	

Dissolution of copper in a ionic liquid/ N_2O_4 mixture. Synthesis and crystal structure of $(BMIm)_2[Cu_2(CF_3COO)_6]$

The next step was the study of the interaction of copper with liquid N_2O_4 in the presence of different ionic liquids. The reaction was carried out at 0-5 °C under conditions excluding the contact of the reaction mixture with air moisture. After dissolution of the metal, the reaction glass ampules were sealed and were kept for crystallization. When the ionic liquid BMIm(CF₃SO₂)₂N was used, blue-green crystals of NO[Cu(NO₃)₃] were formed after seven days according to X-ray powder

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analysis.⁸ In the experiment with BMIm[BF₄], a precipitate of NO[BF₄] was formed.⁷ In the case of BMIm(CF₃COO), a highly hygroscopic precipitate as blue needles was observed. The needles were grown for a month to reach the size sufficient for X-ray diffraction study resulting in the structure determination of $(BMIm)_2[Cu_2(CF_3COO)_6]$ (II) (Table 1). The similarity of the powder diffraction pattern to the theoretical one confirmed the phase purity of this sample.



Fig. 1. Crystal structure of (NO)[BF₄]: (a) projection along the *a* axis with a part of $BF_{4^{-}}$ anions shown as tetrahedra; (b) View along the b axis with some displacement..

According to X-ray structure analysis, crystals of sample II contain a new binuclear copper(II) complex, 1-butyl-3methylimidazolium trifluoroacetocuprate. It consists of 1-butyl-3-methylimidazolium (BMIm⁺) cations and dimeric [Cu₂(CF₃COO)₆]²⁻ anions with two crystallographically independent units. Both copper(II) atoms are coordinated by four bridging trifluoroacetate groups binding the copper ions into a dimer and two terminal CF₃COO groups (one group for each copper atom) (Fig. 2).

The fully ordered coordination polyhedron of the Cu2 atom is a distorted trigonal bipyramid formed by five O atoms of trifluoroacetate groups (Fig. 2, Table 2). The O2, O5 and Cu2 atoms form an axial axis (the O2-Cu2-O5 angle is 175.2°), which is nearly perpendicular to the equatorial plane which includes O4, O8, and O11. The angles in the equatorial plane are considerably different (86, 134, and 140°) because different coordination types of trofluoroacetate groups (bridging and terminals) are involved.

Table 2. Selected bond lengths (Å) and angles (%) The trigonal						
bipyramidal	coordination	environment	of	copper	atoms	in
crystal structure (BMIm) ₂ [Cu ₂ (CF ₃ COO) ₆] (II).						

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	Neighbors of atom Cu1		Neighbors of atom Cu2	
Axial apex	Cu107	1.925(2)	Cu2O5	1.934(2)
	Cu1O3	1.937(2)	Cu2O2	1.939(2)
Equatorial	Cu1O1	2.072(2)	Cu2O11	2.000(2)
apex	Cu1O9	1.976(6)	Cu2O4	2.019(2)
	Cu106	2.154(2)	Cu2O8	2.254(2)
	Cu109A	2.19(3)		
	Cu1010A	2.41(3)		
Axial axis	07Cu103	176.75(8)	O5Cu2O2	175.16(9)
Axial axis –	07Cu101	89.74(9)	O2Cu2O4	88.99(8)
equatorial	07Cu106	88.24(8)	O2Cu2O8	89.62(8)
plane	07Cu109	92.3(3)	O2Cu2O11	92.07(9)
Angles in equatorial plane	O1Cu1O6	134.71(8)	O4Cu2O8	133.70(7)
	O9Cu1O6	89.5(3)	011Cu208	86.42(8)
	O9Cu1O1	135.8(3)	011Cu2O4	139.88(9)
	01Cu109A	82.7(3)		
	O6Cu1O9A	142.4(3)		
Cu1…Cu2	3.150(3)			

The terminal CF₃COO group in the neighborhood of the Cu(1) atom is disordered over two orientations. In the main orientation (occupancy 0.653), this carboxylate group is monodentate (the Cu1-O9 bond length is equal to 1.976(6) Å while distance Cu1…O10 is 2.791(7) Å), and according to Fig. 2 and Table 2, in this case coordination of Cu1 corresponds to the trigonal bipyramid polyhedra very similar like polyhedra of Cu2 atom. In the second orientation (occupancies of O9A and O10A are both 0.347), the carboxylate group exhibits a character of an asymmetric bidentate group (the distances to O9A and O10A atoms are 2.19(3) and 2.41(3) Å, respectively). As a result, for the minor coordination of Cu1, a distorted tetragonal bipyramidal coordination of Cu1 takes place. However, the geometry of the Cu1 polyhedron for the main and minor orientation is about the same without taking into account the additional Cu-O10A bond (Table 2).

The trigonal bipyramid polyhedra of the Cu1 and Cu2 atoms are very much alike. One can see that the axial Cu-O bonds are shorter than the equatorial bonds. Furthermore, one of the three angles in the equatorial plane (89.5 and 86.4° at the Cu1 and Cu2 atoms, respectively) is significantly smaller than the other two angles (133.7, 135.7° and 133.7, 139.9°, respectively). It should be noted that similar geometrical features (a shorter axial and differences in the angles and bond lengths in the equatorial plane) that can be explained by the Jahn-Teller effect are observed for the known cases of the trigonal bipyramid coordination of copper(II) by five O atoms.⁹ For instance, the average lengths of the axial and equatorial bonds in the trigonal bipyramid coordination of the Cu(2) atom in the Cu₂OSO₄ structure ¹⁰ are very close to the corresponding distances found in the structure II. On the other hand, the O-Cu-O angles in $\mathsf{Cu}_2\mathsf{OSO}_4$ are somewhat different: the angles between the axial

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and equatorial planes deviate significantly from 90°, whereas all the three angles in the plane are closer to 120° than the angles in structure II.



Fig. 2. Structure of the binuclear $[Cu_2(CF_3COO)_6]$ anion in the crystal structure of $(BMIm)_2[Cu_2(CF_3COO)_6]$. Fluorine atoms are not shown.

Table 3. Coordination of copper(II) in the known dimeric trifluroacetate complexes: selected bond lengths (Å) and angles (°).

	Cu ₂ (CF ₃ COO) ₄ ¹²		Cu ₂ (CF ₃ COO) ₄](CH ₃ CN) ₂ ¹¹		
Coordination polyhedra	Trigonal bipyramid/ square pyramid		Square pyramid ⁽¹⁾		
Axial apex	CuO4	1.909(2)	Cu1O4	1.964(3)	
	CuO2	1.917(2)	Cu1O3	1.969(2)	
Equatorial	CuO3	1.967(2)	Cu1O2	1.970(2)	
apex	CuO1	2.058(2)	Cu101	1.972(2)	
	CuO1'	2.441(2)	Cu1N1	2.114(2)	
Axial axis	O4CuO2	175.63(9)	O3Cu1O4	164.5(1)	
Axial axis -	-04CuO1'	88.1(1)	O3Cu1N1	98.1(1)	
equatorial	04CuO1	90.8(1)	O3Cu1O2	91.2(1)	
plane	04CuO3	90.3(1)	O3Cu1O1	87.8(1)	
Angles in	O3CuO1	147.07(9)	01Cu102	164.5(1)	
equatorial	01Cu01'	77.07(1)	N1Cu1O2	97.9(1)	
plane	O3CuO1'	135.97(9)	N1Cu1O1	97.5(1)	
Cu…Cu	3.097(1)		2.766(1)		

¹ In this case, the axial axis is chosen randomly as one of the diagonals of the base of the square pyramid.

Due to the presence of four bridged CF_3COO groups, the copper atoms form characteristic dimers resembling a "chinese lantern" (Fig. 2). In this structure, the O atoms of each bridged carboxylate group take the equatorial position with respect to one copper atom and the axial position with respect to the other. The Cu···Cu distance is anomalously elongated (3.15 Å). For comparison, the Cu···Cu distance of 2.77 Å was found for the crystal structure of the dimer complex Cu₂(CF₃COO)₄(CH₃CN)₂ having a tetragonal pyramid coordination of Cu atoms, with the nitrogen atom of an acetonitrile molecule taking the position of the apex of the pyramid (Table 3).¹¹ Such a shortening of the Cu···Cu distance is related to changing geometry of the coordination polyhedron. So, the transfer from the trigonal bipyramid coordination in I to the square pyramid coordination can be represented as a movement of the Skill Skill (OSCA107) and [O2Cu2O5] toward each other, with a simultaneous increase of the angles O1Cu1O6 and O4Cu2O8 (Fig. 2).

It is interesting to note that the dimeric fragment (the "chinese lantern") in the structure of anhydrous copper(II) trifuoroacetate $Cu(CF_3COO)_2$ characterized by the Cu…Cu distance of 3.10 Å ^{12, 13} is an intermediate form between a "classical" chinese lantern and the trifluoroacetate complex studied in our work The coordination of the copper atom in the $Cu(CF_3COO)_2$ structure can be described as a distorted trigonal bipyramid (Table 3), whereas the bridging trifluoroacetate groups are located in the axial positions. As a result, the dimers form an infinite chain.¹² However the authors of ¹³ consider the polyhedron of a copper atom as a distorted square pyramid. This assumption is based on the elongation of the Cu-O distance to one of the equatorial O atoms approaching 2.44 Å.

Conclusions

A new synthetic approach was successfully used for the preparation of solutions of anhydrous nitrates by interaction of dinitrogen tetraoxide with metals in a medium of ionic liquids. It was expected and it was found that an ionic liquid will not only assist in dissociation of N_2O_4 into NO^+ and NO_3^- , which is a necessary prerequisite for the dissolution of a metal, but will also take part in the formation of complexes as a source of cations and/or anions.

Depending on the composition of the ionic liquid, different crystalline products can be isolated from the solution, with the nature of the anion of the ionic liquid playing the major role. So, the bis(triflate) imide anion is a weaker field anion as compared to the nitrate anion, whereas trifluoroacetate is a stronger field anion. As a result, crystals of nitrosonium nitratocuprate are formed from a solution of copper(II) nitrate in BMIm(CF₃SO₂)₂N, while the trifluoroacetate dimeric complex is formed from a solution of BMIm(CF₃COO). In the case of BMIm(BF₄), NOBF₄ is the least soluble and, therefore, this salt is precipitated from the solution.

In general, the results obtained provide evidence for the efficient use of ionic liquids for inorganic syntheses. Note that earlier ionic liquids have been already proven as benign media in organic syntheses. Thus, the nature of the ionic liquid (Cat⁺An⁻) in the interaction of copper with N₂O₄ governs the formation of a variety of products, including both NO⁺An⁻ and Cat₂[Me₂An₆]. The application of this approach in studying the interaction of other metals will presumably result in the new complexes with interesting catalytic and optical properties, in line with the strategy of synthesis of complex molecular systems and hybrid materials¹⁴.

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Notes and references

‡ Experimental section

Materials

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A Cu powder (99.99% purity) and Pb(NO₃)₂ (99.8% purity) were used. The ionic liquids (BMIm)A (A⁼ [BF₄]⁻, (CF₃SO₂)₂N⁻, CF₃COO⁻) were prepared by anion exchange of MBImCl with the corresponding Li salts with further purification and drying. The water content was below 50 ppm as controlled by the Fischer method.

XRD analysis was performed using a DRON-4-07 reflecting type diffractometer with Cu K α radiation and scintillation detector. In order to prevent the contact with air during the X-ray diffraction pattern measurements, the hygroscopic samples were placed in a quartz sample holder in an atmosphere of dry argon and were sealed with a polypropylene film. The assessment of the diffraction patterns and phase analysis were performed using an STOE WinXPow software.

Single crystal XRD studies were performed for single crystals of (NO)[BF₄] and (BMIM)₂[Cu₂(TFA)₆] using an IPDS diffractometer (Stoe) with monochromatized Mo K_α radiation (λ = 0.71073 Å). The structures were solved and anisotropically refined with the SHELX package. The details of the data collection and structure refinement are given in Table 1. Selected interatomic distances and angles for (BMIM)₂[Cu₂(TFA)₆] are summarized in Table 2.

Liquid N₂O₄ was prepared by thermal decomposition of lead nitrate according to the procedure described elsewhere.¹⁵ Lead nitrate was preliminarily heated at 150°C for 3 h to remove traces of water and was decomposed in a flask supplied with a drying column with P₂O₅ and a direct assending condenser with a trap cooled to 0°C. A brown liquid (the boiling point of liquid N₂O₄ is 20°C) formed a crystalline specimen upon cooling to below -10°C, which corresponded to the melting point of N₂O₄. The absence of a blueish color confirmed the absence of traces of water and NO in N₂O₄.² Portions (2-4 g) of dinitrogen tetraoxide synthesized were sealed in glass ampoules for further experiments.

Interaction of N₂O₄ with ionic liquids. Synthesis of NO[BF₄]. In the case of each of the three ionic liquids studied in this work, the cooled (10°C) portion of N₂O₄ (1 g or 0.5 cm³) and an equal volume of the ionic liquid under study (10°C) were placed in a glass ampoule with magnetic stirring bars, the ampoule was sealed and the content was stirred on a magnetic stirrer (a hot plate) at 35-40°C for 1 week. Nitrosonium tetrafluoroborate was prepared by the interaction of N₂O₄ with BMIm[BF₄] (IL1). In this case, the sealed ampoule was kept for 1.5 months in order to produce large crystals suitable for X-ray structure analysis. The crystals were isolated by centrifugation, then the ampoule was opened in a dry glove box and the crystals of NO[BF₄] are rapidly decomposed in air in the presence of moisture, they are dissolved in water with evolution of NO and NO₂ gases, which is typical for nitrosonium salts.

Dissolution of copper in mixtures of an ionic liquid and dinitrogen tetraoxide. Synthesis of (*BMIm*)₂[Cu₂(CF₃COO)₆]. A loading of copper powder was placed in a glass ampoule, cooled to 0°C and a mixture of dinitrogen tetraoxide and an ionic liquid was added at 0°C. The ampoule supplied with a drying column with P₂O₅ was placed in a Dewar vessel with ice. For all the studied ionic liquids, dissolution of copper was observed with evolution of NO. The dissolution process proceeded for several days, then the reaction mixture was allowed to warm up to room temperature. An excess of unreacted dinitrogen tetraoxide was removed from the solutions by keeping them at room temperature, the ampoules were sealed and kept for crystallization. After 1-4 weeks, crystals were precipitated in all the cases. They were separated by centrifugation, the ampoules were opened in a dry glove box and the crystals were kept on a porous filter to remove the liquid. The crystals obtained were studied by powder and single crystal X-ray diffraction.

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- 4 Caution! One should use mixtures of N_2O_4 with organic compounds with extreme precautions, because potentially

explosive nitration products can be formed. Such mixtures must not be heated without detailed studies and preliminary small-scale experiments.

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$$N_2O_4 + IL \rightarrow NO^+ + NO_3^-$$
, IL=ionic liquid
 $BMIm^+BF_4^- + N_2O_4 \rightarrow BMIm^+NO_3^- + NO^+BF_4^+$
 $Cu + BMIm^+(CF_3SO_2)_2N^- + N_2O_4 \rightarrow NO^+[Cu(NO_3)_3]^-$
 $Cu + BMIm^+CF_3COO^- + N_2O_4 \rightarrow (BMIm)_2[Cu_2(CF_3COO)_6]$ (a "chinese lantern" structure)

