One-Step Syntheses of Polyhalogenometal Complexes by Direct Dissolution of the Metals in Halogen-Halide-Acetonitrile Systems

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Polyhalogeno complexes of $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{I}}$, $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{Pd^{IV}}$, $\mathrm{Ag^{I}}$, $\mathrm{Sn^{II}}$, $\mathrm{Sn^{IV}}$, $\mathrm{Au^{I}}$, and $\mathrm{Au^{III}}$ are synthesized in one step by dissolving the corresponding metals in halogen-halide-acetonitrile systems.

We recently[1] found that a series of organic solvent systems containing an elementary halogen ($\mathrm{X_2}$, X=Cl, Br, or I) and a halide ($\mathrm{Q^+X^-}$; Q=Na, $[\mathrm{NR_4}]$, etc.) exhibit high abilities comparable to *aqua regia* in dissolving noble metals. These new organic solvent systems are much safer than conventional solvents and serve as a solvent for various metals. We describe here a new application of these organic systems to the one-step synthesis of polyhalogenometal complexes which are not only essential to coordination chemistry[2] but also useful as two-dimensional magnets,[3] solid conductors,[4] liquid media for chemichal reactions,[5] and catalysts.[6] Most conventional methods for synthesizing such polyhalogenometal complexes involve the reaction of the corresponding metal halides, which are hygroscopic or deliquescent, with $\mathrm{Q^+X^-}$. Moreover, these methods often require the substitution reaction of the halide ions, and, for complexes containing lower valent metals, the reduction of the metal ions resulting in a significant deposition of the metals.[7] By the present method, various polyhalogenometal complexes including those of lower valent metals can be easily synthesized in high yield by dissolving the metals in the organic solvent systems.

A piece of 0.2 mm diameter metal wire (ca.1.2 mmol) was added to an organic solvent system consisting of $\mathrm{X_2}$, a tetraethylammonium halide ($[\mathrm{NEt_4}]^+\mathrm{X}^-$), and acetonitrile (10 g) and allowed to dissolve under refluxing at 82 ℃ until the weight of the metal remainder no longer decreased. The amounts of $[\mathrm{NEt_4}]^+\mathrm{X}^-$ and $\mathrm{X_2}$ used were those neccesary to dissolve 1 mmol of the metal and to give the expected composition of the product calculated from the following stoichiometry.

$$a\mathrm{M} + b\mathrm{X_2} + c[\mathrm{NEt_4}]^+\mathrm{X}^- \rightarrow [\mathrm{NEt_4}]^+_c[\mathrm{M}_a\mathrm{X}_{2b+c}]^{c-} \qquad (1)$$

In the cases using Fe, Cu, Pd, Sn, and Au which exhibit two different valences, they initially gave the higher valent metals until $\mathrm{X_2}$ was completely consumed, then the lower valent metals were formed by the following retro-disproportionation reaction.

$$p\mathrm{M}^{n} + q\mathrm{M}^{0} \rightarrow (p+q)\,\mathrm{M}^{m} \qquad \text{where } pn=(p+q)\,m \qquad (2)$$

Therefore, in order to synthesize complexes containing higher valent metals, it is required to use as much of the metal as it takes to consume $\mathrm{X_2}$. For the exceptional case of $\mathrm{Au^{III}}$ complexes, dissolution of gold ceased at the point where $\mathrm{X_2}$ and $[\mathrm{NEt_4}]^+\mathrm{X}^-$ had been simultaneously used up.

After thus saturated with the dissolved metal, the solution was separated from the metal remainder and cooled to form a crystalline product, which was then separated and dried. Alternatively, the solution was evaporated to the crude product, which was then purified by recrystallization from a suitable solvent. The structure of the complexes produced and the valence of the metals were evaluated on the basis of their composition determined by their elemental analyses and, in some cases, their melting point compared with those described in the literatures.[7]

Table 1. Polyhalogenometal complexes obtained by dissolving the metals (M) in $\mathrm{X_2}/[\mathrm{NEt_4}]^+\mathrm{X}^-$/acetonitrile (10 g, 12.8 ml)[a]

M[b]	$\mathrm{X_2}/[\mathrm{NEt_4}]^+\mathrm{X}^-$ mmol / mmol	Chemical formula[c] Solvent for recrystallization mp Yield[d]		
		X=Cl	X=Br	X=I
Fe	1/3	$[\mathrm{Fe^{II}Cl_4}]^{2-}$ MeCN (4.5 ml) 250-260 ℃ 54%	A	A
Fe*	1.5/2	$[\mathrm{Fe^{III}Cl_4}]^{-}$ EtOH (30 ml) 190-220 ℃ 93%	$[\mathrm{Fe^{III}Br_4}]^{-}$ EtOH (100 ml) 240-270 ℃ 93%	A
Ni	1/3	$[\mathrm{Ni^{II}Cl_4}]^{2-}$ MeCN (6.4 ml) >300 ℃ 60%	$[\mathrm{Ni^{II}Br_4}]^{2-}$ MeCN (2.6 ml) >300 ℃ 67%	A
Cu	0.5/1	$[\mathrm{Cu^{I}Cl_2}]^{-}$ $\mathrm{Me_2CO}$ (10 ml) - $\mathrm{Et_2O}$ (40 ml) 230 ℃ (dec.) 80%	$[\mathrm{Cu^{I}Br_2}]^{-}$ $\mathrm{Me_2CO}$ (10 ml) - $\mathrm{Et_2O}$ (40 ml) 148-149 ℃ 95%	$[\mathrm{Cu^{I}{}_2I_3}]^{-}$ MeCN (10 ml) - EtOH (10 ml) 183-190 ℃ 65%
Cu*	1/3	$[\mathrm{Cu^{II}Cl_4}]^{2-}$ EtOH (10 ml) 243-247 ℃ 91%	$[\mathrm{Cu^{II}Br_4}]^{2-}$ EtOH (20 ml) 225-227 ℃ 95%	$[\mathrm{Cu^{I}{}_2I_3}]^{-}$ MeCN (10 ml) - EtOH (10 ml) 183-190 ℃ 71%
Zn	1/3	$[\mathrm{Zn^{II}Cl_4}]^{2-}$ EtOH (40 ml) >300 ℃ 94%	$[\mathrm{Zn^{II}Br_4}]^{2-}$ EtOH (30 ml) >300 ℃ 97%	$[\mathrm{Zn^{II}I_4}]^{2-}$ EtOH (16 ml) - MeOH (4 ml) >300 ℃ 82%
Pd	1/2	$[\mathrm{Pd^{II}Cl_4}]^{2-}$ MeCN (12.8 ml) 240 ℃ (dec.) 62%	$[\mathrm{Pd^{II}Br_4}]^{2-}$ MeCN (3 ml) 276 ℃ (dec.) 58%	$[\mathrm{Pd^{II}{}_2I_6}]^{2-}$ MeCN (12.8 ml) 199-201 ℃, 68%
Pd	1/1	$[\mathrm{Pd^{II}{}_2Cl_6}]^{2-}$ MeOH (10 ml) 178 ℃ 87%	$[\mathrm{Pd^{II}{}_2Br_6}]^{2-}$ EtOH (15 ml) - $\mathrm{Me_2CO}$ (15 ml) 142 ℃ 84%	$[\mathrm{Pd^{II}{}_2I_6}]^{2-}$ MeCN (2.6 ml) 201 ℃ 86%
Pd*	2/2	$[\mathrm{Pd^{IV}Cl_6}]^{2-}$ MeCN (12.8 ml) 240 ℃ (dec.) 86%	A	$[\mathrm{Pd^{II}{}_2I_6}]^{2-}$ MeCN (12.8 ml) 200 ℃ 77%

Ag	0.5/3	A	$[\mathrm{Ag^{I}Br_2}]^-$ MeCN (5.1 ml) 168-171 °C 70%	$[\mathrm{Ag^{I}I_2}]^-$ MeCN (12.8 ml) 189 °C 87%
Ag	0.5/1	B	$[\mathrm{Ag^{I}_2Br_3}]^{-\,e}$ MeCN (12.8 ml) 227-229 °C 84%	$[\mathrm{Ag^{I}_2I_3}]^{-\,e}$ MeCN (12.8 ml) 233 °C 57%
Sn	1/2	A	A	$[\mathrm{Sn^{II}I_3}]^-$ MeCN (12.8 ml) 160-180 °C (dec.) 75%
Sn*	2/4	$[\mathrm{Sn^{IV}Cl_6}]^{2-\,e}$ MeCN (12.8 ml) - MeOH (5.1ml) >300 °C 51%	$[\mathrm{Sn^{IV}Br_6}]^{2-\,e}$ MeCN (12.8 ml) >300 °C 94%	$[\mathrm{Sn^{IV}I_6}]^{2-}$ MeCN (12.8 ml) 160 °C 73%
Au	0.5/1	$[\mathrm{Au^{I}Cl_2}]^-$ EtOH (6.4 ml) - $\mathrm{Et_2O}$ (12.8ml) 71-74 °C 42%	$[\mathrm{Au^{I}Br_2}]^-$ EtOH (2 ml) - $\mathrm{Me_2CO}$ (0.2ml) 88-89 °C 79%	$[\mathrm{Au^{I}I_2}]^-$ EtOH (5 ml) 105 °C 85%
Au	1.5/1	$[\mathrm{Au^{III}Cl_4}]^-$ EtOH (70 ml) 244 °C (dec.) 87%	$[\mathrm{Au^{III}Br_4}]^-$ EtOH (120 ml) 203-215 °C 85%	B

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[a] A: No pure complex was isolated. B: The metal was not dissolved enough. [b] Excess (ca. 1.2 mmol) of the metal was used except for the cases asterisked in which just 1 mmol of the metal was used. [c] The cationic part ($[\mathrm{NEt_4}]^+$ or $[\mathrm{NEt_4}]^+_2$) is ommited. [d] Based on the metal dissolved. [e] The complex was deposited during metal dissolution.

As shown in Table 1, various polyhalogenometal complexes were successfully obtained by using eight common metals. In certain cases, the use of excess $[\mathrm{NEt_4}]^+\mathrm{X}^-$ resulted in an appreciably high yield. It should be noted that the ratio $\mathrm{X_2/M}$ determines the valence of the metal ($\mathrm{Fe^{II}}$ or $\mathrm{Fe^{III}}$, $\mathrm{Cu^{I}}$ or $\mathrm{Cu^{II}}$, $\mathrm{Pd^{II}}$ or $\mathrm{Pd^{IV}}$, $\mathrm{Sn^{II}}$ or $\mathrm{Sn^{IV}}$, and $\mathrm{Au^{I}}$ or $\mathrm{Au^{III}}$). Exceptional failure in synthesizing the polyiodo complexes of the higher valent metals, $\mathrm{Cu^{II}}$ and $\mathrm{Pd^{IV}}$, in the $\mathrm{I_2}$-containing systems would be due to the poor oxidizing ability of the systems. On the other hand, the ratio $[\mathrm{NEt_4}]^+\mathrm{X}^-/\mathrm{X_2}$ effects the nuclear-multiplicity of the $\mathrm{Pd^{II}}$ and $\mathrm{Ag^{I}}$ complexes. Thus, the mononuclear and dinuclear complexes were obtained with the larger and smaller ratios $[\mathrm{NEt_4}]^+\mathrm{X}^-/\mathrm{X_2}$, respectively. In some cases, we failed in isolating pure complexes because of difficulty in crystallization or contamination with the other complex. Crystalline products expected to be the polybromo complexes of $\mathrm{Fe^{II}}$ and $\mathrm{Sn^{II}}$ were too sensitive to air to be analysed. From the solution intended to give the polyiodo $\mathrm{Au^{III}}$ complexes, only metallic gold was deposited upon cooling.[8]

Polyhalogeno complexes of other metals (Mn, Co, Cd, Hg, etc.) and those with other cations including quaternary ammonium ions having long alkyl chains were also easily synthesized in one step in a similar manner.

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