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Gas-phase Reactions of Bis(dipivaloylmethanato)metal(II) Complexes with Electrons, Halide Ions and Radicals

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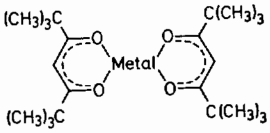
Abstract

The negative chemical ionization (NCI) mass spectra of a series of bis(2,2,6,6-tetramethylheptane-3,5-dionato)metal(II) complexes [metal = Co, Ni, Cu, Zn] obtained using the halogenated reagent gases, NF_3, CF_2Cl_2 and CF_3Br, are presented. Thermalized electrons are captured by the Co, Ni and Cu complexes to produce molecular ions in which the oxidation state of the metal has been reduced. Lewis acid–base addition of halide ions to the metal to produce adduct ions occurs with each of the metal complexes. Reactions between radicals and the complexes also occur to produce adduct molecules which may be ionized by thermalized electrons or halide ions in the same manner as the parent complexes. Halogen radicals react by ligand displacement and homolytic substitution of the ligand while halogenated methyl radicals undergo oxidative-addition to the metal. Clustering reactions to produce ions containing two metal atoms also occur.

Introduction

The technique of negative chemical ionization (NCI) mass spectrometry offers considerable utility as a means for investigating the gas-phase chemistry of metal coordination compounds under solvent-free conditions [1]. In the presence of moderating gases, interactions of low energy electrons with metal complexes may be examined [1–3] and with transition metal complexes these interactions often lead to reduction of the metal [2, 3]. By appropriate selection of reagent gases, reactions of metal complexes with a range of nucleophiles such as halide ions may be studied [4–6]. With such systems a variety of ion/molecule reactions have been identified, including nucleophilic addition, proton abstraction and nucleophilic ligand displacement [4–6]. Reactions between metal complexes and radicals may also be investigated by examining the ionized products of these processes [4–8]. Oxidative-addition of alkyl radicals to cobalt(II) complexes [5, 7], insertion reactions of methylidyne radicals [8] and ligand displacement by halogen radicals [4, 5] have all been identified in NCI plasmas.



In this paper we report on a study of the gas-phase negative ion chemistry of a series of bis(dipivaloylmethanato)metal(II)[†] complexes (metal = Co, Ni, Cu, Zn) (I) in the halogenated reagent gas plasmas of NF_3, CF_2Cl_2 and CF_3Br. This work was undertaken as part of a systematic study into the gas-phase negative ion chemistry of transition metal(II) coordination complexes in the presence of electrons, nucleophiles and radicals. Bis(dipivaloylmethanato)metal(II) [herein referred to as metal$(dpm)_2$] complexes are of interest in that they exhibit Lewis acid properties [9, 10] as well as metal-dependent oxidation–reduction chemistry in solution [10], and may therefore be expected to be reactive towards a variety of species in the gas phase. Reactions of several of these complexes with low-energy electrons [2, 3, 8] and hydrocarbon radicals [7, 8] have been examined previously. NF_3, CF_2Cl_2 and CF_3Br are convenient sources of gas-phase fluoride, chloride and bromide ions respectively, as well as thermalized electrons and a variety of radicals [4, 5]. Hence, the NCI mass spectra of metal complexes obtained with these reagent gases facilitate the identification of negative ion products and their formation mechanisms which arise from a range of electron/molecule, ion/molecule and radical/molecule processes.

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[†] IUPAC nomenclature: bis(2,2,6,6-tetramethylheptane-3,5-dionato)metal(II).

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Experimental

The metal(dpm)$_2$ complexes were prepared by established procedures [11] and purified by recrystallization from ethanol followed by vacuum sublimation. The sublimed complexes gave satisfactory analyses. Commercially available dipivaloylmethane (Fairfield Chemical Co., Blythewood, S.C., U.S.A.) was used without further purification in these preparations.

The NCI mass spectra were obtained with a VG MM-16F single focusing mass spectrometer fitted with a dual EI/CI ion source (VG Analytical Instruments, Altrincham, Cheshire, UK). The principal instrumental parameters used were as follows: ion source pressure, 0.1 torr; filament emission current, 500 μA; primary electron energy, 50 or 100 eV; repeller voltage, 0 to -1 V; ion accelerating voltage, -4 kV. Ion source temperatures of 90–150 °C were used to vaporize the metal complexes from a silica cup placed directly into the ion source. Filament emission settings of 100, 200, 500 and 1000 μA were used to identify ions arising from radical reactions [12, 13].

NF_3 (Spectra Gases, Newark, N.J., U.S.A.), CF_2Cl_2 and CF_3Br (Pacific Chemical Industries, Sydney, N.S.W., Australia) were used as reagent gases as purchased. In the absence of added analyte molecules, the NCI mass spectra of NF_3, CF_2Cl_2 and CF_3Br consisted primarily of $[F]^-$, $[Cl]^-$ and $[Br]^-$, respectively (*ca.* 99% of the total ion current).

An isotopic cluster simulation program [14] was used to confirm the empirical formulae of ion assignments and to deconvolute overlapping isotopic clusters. Apart from $[L]^-$, the origin of most of the organic fragment ions such as $[L + X - H]^-$ was not established, but it was noted that the relative abundances of these ions generally increased with increasing filament emission current. Reactions of plasma radicals with solid metal complex on the insertion probe is likely to have occurred prior to vaporization in some instances.

Results and Discussion

Chemical ionization (CI) plasmas generated from halogenated reagent gases contain a variety of reactive species which may influence the types of ions formed when analyte molecules are introduced into these plasmas. An appraisal has been given previously of the physical and chemical processes leading to the formation and destruction of important positive ions, negative ions, halogen atoms, halogenated methyl radicals and thermalized electrons in CI plasmas generated from NF_3, CF_2Cl_2 and CF_3Br [5]. These plasmas contain abundant populations of the halide ions, fluoride, chloride and bromide respectively, formed from the reagent gases by dissociative capture of thermalized electrons. As not all of the thermalized electrons formed initially are captured by the reagent gas, some are available for reaction with analyte molecules. Also present are reactive radicals arising from a number of processes [5].

Metal complexes introduced into the NF_3, CF_2Cl_2 and CF_3Br plasmas undergo a variety of reactions leading to the formation of a range of metal-containing and organic ions. Upon exiting the ion source by flow or diffusion, these ions may be accelerated, mass analysed and detected in the conventional way to yield positive or negative ion CI mass spectra depending on the polarity of the accelerating voltage and magnetic sector. Table I lists the assigned formulae of the ions identified in the NF_3, CF_2Cl_2 and CF_3Br NCI mass spectra of the metal(dpm)$_2$ complexes along with the percentage of the total ion current in each mass spectrum carried by these ions.

Each of the NCI mass spectra of the cobalt, nickel and copper complexes contain a molecular ion, $[\mathrm{metal^{I}L_2}]^-$, formed by resonance capture of a thermalized electron into the lowest unoccupied or singly occupied molecular orbital [1–3] As resonance electron capture to give a 'long-lived' [15] molecular ion can only occur if the molecule has a positive electron affinity, an excited molecular ion is formed initially [16]; reaction (1). Stabilization of the excited molecular ion by collision with reagent gas molecules, M, as represented in reaction (2) is necessary to prevent autodetachment of the captured electron or the occurrence of rearrangement/fragmentation processes [1, 16]. It is envisaged that the cobalt, nickel and copper complexes each capture the electron into a metal-based orbital, thereby effecting a decrease in the oxidation state of the metal [2, 3]. With $3d^7$–$3d^9$ electron configurations, these metals possess unoccupied or singly occupied 3d orbitals which may accommodate the captured electron. It has been determined that the relative ion currents generated from these complexes by resonance electron capture, using methane as an electron energy moderating/collisional stabilization gas, decreases in the order, Cu (40) > Ni (10) > Co (1) [2] This trend is probably a reflection of the increasing electron affinities of the complexes upon going from cobalt to copper across the periodic table, and accounts for the high percentage of the total ion current carried by the molecular ion in the mass spectra of the copper complex. Due to the $3d^{10}$ configuration of zinc(II), the zinc complex does not form a long-lived and thus detectable molecular ion.

$$\mathrm{metal^{II}L_2} + e^- \longrightarrow [\mathrm{metal^{I}L_2}]^{-*} \tag{1}$$

$$[\mathrm{metal^{I}L_2}]^{-*} + \mathrm{M} \longrightarrow [\mathrm{metal^{I}L_2}]^- + \mathrm{M} \tag{2}$$

$$[\mathrm{metal^{I}L_2}]^{-*} \longrightarrow \mathrm{metal^{I}L} + [\mathrm{L}]^- \tag{3}$$

TABLE I. Percentage of the Total Ion Current (TIC) Carried by Ions in the NF_3, CF_2Cl_2 and CF_3Br NCI Mass Spectra of the Bis(dipivaloylmethanato)metal(II) Complexes[a–c]

Ion	Reagent gas/metal											
	NF_3				CF_2Cl_2				CF_3Br			
	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn	Co	Ni	Cu	Zn
$[\mathrm{Metal}^{\mathrm{II}}{}_2\mathrm{L}_y\mathrm{X}_z]^-$ [d]								5	4			7
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{A}]^-$ [e]	20	9	3	9	4	5	3	0.3	2	0.4		0.2
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}_2 - \mathrm{H}]^-$	0.3	0.5	0.2	0.3	5			0.4	3			0.2
$[\mathrm{Metal}^{\mathrm{III}}\mathrm{L}_2\mathrm{RX}]^-$					0.4				20			
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{R}]^-$									2			
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^-$	27	11	30	32	55	73	56	49	33	91	38	55
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X} - 2\mathrm{H}]^-$	0.6		0.3	0.8	2				1		6	0.8
$[\mathrm{Metal}^{\mathrm{I}}\mathrm{L}_2]^-$	7	0.7	4		0.2	0.4	6		0.3	0.1	28	
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{LX}_2]^-$	0.7	0.3	0.6	1	9	3	4	28	4	7	6	29
$[\mathrm{Metal}^{\mathrm{I}}\mathrm{LX}]^-$			0.4				3				4	1
$[\mathrm{Metal}^{\mathrm{II}}\mathrm{X}_3]^-$					6	0.2	1	11	17			6
$[\mathrm{Metal}^{\mathrm{I}}\mathrm{X}_2]^-$							7				15	0.3
$[\mathrm{L} + \mathrm{A}']^-$ [f]	6	2	4	4	15	14	8	5	8	0.6	2	0.2
$[\mathrm{L} + \mathrm{X} - \mathrm{H}]^-$	1	2	4	0.6	2	2	2	0.5	3			0.1
$[\mathrm{L}]^-$	26	57	18	40	1	2	11	0.8	2	0.2	0.5	0.2
[Ligand fragments]$^-$ [g]	10	17	35	10								
$[\mathrm{X}]^-$/TIC	0.4	0.4	0.4	0.3	1.0	1.8	1.9	0.3	3.0	2.1	1.3	0.9
Temperature (°C)	115	150	130	110	120	140	140	100	120	145	150	95

[a] All isotopes of all atoms included. [b] L corresponds to $C_{11}H_{19}O_2$; X represents F, Cl and Br in NF_3, CF_2Cl_2 and CF_3Br, respectively. [c] R corresponds to CF_2Cl and CF_3 in CF_2Cl_2 and CF_3Br, respectively. [d] $y + z = 5$. [e] A represents HX_2, L, (L + X – H) and (ligand fragments). [f] A′ is primarily HX and X_2. [g] Primarily $[\mathrm{L} - 2\mathrm{H}]^-$, $[\mathrm{L} - \mathrm{CH}_4]^-$ and $[\mathrm{L} - \mathrm{C}_4\mathrm{H}_{10}]^-$.

A proportion of the excited $[\mathrm{metal}^{\mathrm{I}}\mathrm{L}_2]^{-*}$ ions may fragment prior to collisional stabilization to produce the free ligand anion, $[\mathrm{L}]^-$, reaction (3), and metastable peaks arising from this fragmentation have been identified previously [2, 3]. This reaction constitutes the primary source of $[\mathrm{L}]^-$ in the CF_2Cl_2 and CF_3Br NCI mass spectra. The comparatively high relative abundances of $[\mathrm{L}]^-$ in the NF_3 mass spectra arise because of an additional formation mechanism, discussed later, in the NF_3 plasma.

In competition with resonance electron capture, the metal complexes react with the abundant halide ions in the plasmas to produce adduct ions of the form, $[\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^-$. The nucleophile, X, corresponds to F, Cl and Br, respectively, in the NF_3, CF_2Cl_2 and CF_3Br NCI mass spectra. These adduct ions are the most abundant ions in the CF_2Cl_2 and CF_3Br mass spectra of each of the metal complexes and are also prominent in the NF_3 mass spectra. It is noteworthy that although the zinc complex does not undergo resonance electron capture, it does react readily with halide ions. Nucleophilic addition of a halide ion to the metal complexes is likely to entail direct coordination of the halide ion to the metal since the Lewis acidity of bis(β-ketoenolato)metal(II) complexes [9, 10] and the Lewis basicity of halide ions in solution [17] are well established. As with resonance electron capture, it is probable that the exothermicity of nucleophilic halide addition causes the adduct ions to be excited until the excess energy is removed by collisions with reagent gas molecules, reactions (4) and (5).

$$\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2 + [\mathrm{X}]^- \longrightarrow [\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^{-*} \qquad (4)$$

$$[\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^{-*} + \mathrm{M} \longrightarrow [\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^- + \mathrm{M} \qquad (5)$$

$$[\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^{-*} \longrightarrow \mathrm{metal}^{\mathrm{II}}\mathrm{LX} + [\mathrm{L}]^- \qquad (6)$$

A proportion of the $[\mathrm{metal}^{\mathrm{II}}\mathrm{L}_2\mathrm{X}]^{-*}$ ions fragment to produce the free ligand ion and a molecule of $\mathrm{metal}^{\mathrm{II}}\mathrm{LX}$, reaction (6), a process which occurs in competition with collisional stabilization. The combined effect of reactions (4) and (6) is ligand displacement where a halide ion displaces a dpm anion, $[\mathrm{L}]^-$, from the coordination sphere of the metal. Although deficiencies in the thermochemical data base do not allow the enthalpy change for this particular displacement to be calculated, enthalpy calculations with the related bis(acetylacetonato)metal(II) complexes [5] have indicated that nucleophilic ligand displacement is exothermic with the fluoride ion but substantially endothermic with chloride and bromide ions. This accounts for the high abundance of $[\mathrm{L}]^-$ in the NF_3 mass spectra of the complexes. Gas-phase nucleophilic ligand displacement from transition-metal coordination complexes is of interest in that it may be similar mechanistically to nucleophilic substitution involving main group elements such as silicon and phosphorus [18]. To date, gas-phase S$_N$2 reactions involving transition metal coordination compounds have not been studied.

Apart from the halide adduct ions, the mass spectra also contain adduct ions of the general form, [metal^{II}L$_2$A]$^-$, where A corresponds to HX$_2$, L, (L + X − H) and ligand fragments such as (L − C$_4$H$_{10}$). As with the halide adduct ions, formation of these adduct species is attributed to a nucleophilic addition process, reaction (7), because an [A]$^-$ ion is present in each of the mass spectra in which the corresponding [metal^{II}L$_2$A]$^-$ adduct is observed.

$$\text{metal}^{\text{II}}\text{L}_2 + [\text{A}]^- \xrightarrow{\text{M}} [\text{metal}^{\text{II}}\text{L}_2\text{A}]^- \tag{7}$$

A number of ions in the mass spectra owe their origins to reactions between the metal complexes and radicals in the plasmas. The neutral products of these radical/molecule reactions are detected as negative ions once they are ionized by either resonance electron capture or nucleophilic halide addition. It has been established that the ionized products of radical/molecule reactions may be prominent in NCI mass spectra, even though these reactions are typically several orders of magnitude slower than electron/molecule and ion/molecule processes, because the radical concentration in the plasma may be orders of magnitude greater than the electron and ion concentrations [12, 13]. Ions arising from radical reactions may be identified by increasing the filament emission current, whereupon the abundance of these ions will increase relative to other ions such as the molecular ion [12]. This type of emission dependence has been observed with all the ions in Table I which are attributed to radical/molecule reactions.

Formation of the ions, [metal^{I}LX]$^-$, [metal^{II}LX$_2$]$^-$, [metal^{I}X$_2$]$^-$ and [metal^{II}X$_3$]$^-$, where one or both of the dmp ligands have been displaced from the metal, is attributed to reactions between halogen radicals and the metal complexes prior to ionization [4, 5]. In competition with the ionization processes described previously, the metal complexes react with halogen radicals according to reaction (8). This reaction entails the transfer of an electron from the dpm ligand to the atomic halogen to produce a halide ion which becomes coordinated to the metal and a dpm radical, L·, which is displaced. Radical-induced ligand displacement in this manner is driven by the exceptionally high electron affinities of halogen atoms. Ionization of the resultant metal^{II}LX molecule by resonance electron capture and nucleophilic halide addition accounts for the formation of [metal^{I}LX]$^-$ and [metal^{II}LX$_2$]$^-$, respectively; reactions (9) and (10). Alternatively, metal^{II}LX may undergo an analogous reaction with a second halogen radical to produce a metal halide molecule, metal^{II}X$_2$; reaction (11). Ionization of the metal halide by resonance electron capture and nucleophilic halide addition affords the ions, [metal^{I}X$_2$]$^-$ and [metal^{II}X$_3$]$^-$, respectively; reactions (12) and (13). In contrast, solvent molecules markedly influence reactions between radicals and bis(β-ketoenolato)metal(II) complexes since homolytic substitution reactions at the ligand tend to predominate in solution [11].

$$\text{metal}^{\text{II}}\text{L}_2 + \text{X}\cdot \longrightarrow \text{metal}^{\text{II}}\text{LX} + \text{L}\cdot \tag{8}$$

$$\text{metal}^{\text{II}}\text{LX} + e^- \xrightarrow{\text{M}} [\text{metal}^{\text{I}}\text{LX}]^- \tag{9}$$

$$\text{metal}^{\text{II}}\text{LX} + [\text{X}]^- \xrightarrow{\text{M}} [\text{metal}^{\text{II}}\text{LX}_2]^- \tag{10}$$

$$\text{metal}^{\text{II}}\text{LX} + \text{X}\cdot \longrightarrow \text{metal}^{\text{II}}\text{X}_2 + \text{L}\cdot \tag{11}$$

$$\text{metal}^{\text{II}}\text{X}_2 + e^- \xrightarrow{\text{M}} [\text{metal}^{\text{I}}\text{X}_2]^- \tag{12}$$

$$\text{metal}^{\text{II}}\text{X}_2 + [\text{X}]^- \xrightarrow{\text{M}} [\text{metal}^{\text{II}}\text{X}_3]^- \tag{13}$$

Halogen radicals also react with the metal complexes by homolytic displacement of a dpm hydrogen atom to produce a molecule of the form, (metal^{II}L$_2$X − H), reaction (14). Equivalent species have been identified as the products of reaction between electrophilic species and metal β-ketoenolate complexes in solution. In view of the established substitution chemistry of metal β-ketoenolate complexes in solution, it is envisaged that this substitution takes place at the methine carbon atom of one of the ligands [10]. The occurrence of reaction (14) is indicated by formation of the ion produced from (metal^{II}L$_2$X − H) by nucleophilic halide addition, [metal^{II}L$_2$X$_2$ − H]$^-$, reaction (16). Resonance electron capture by the (metal^{II}L$_2$X − H) molecule would produce an ion of the form, [metal^{I}L$_2$X − H]$^-$; reaction (15). This ion, which may have been of low relative abundance, was not identified definitively due to the presence of the abundant [metal^{II}L$_2$X]$^-$ ion one *m/z* unit higher in the mass spectra and a [metal^{II}L$_2$X − 2H]$^-$ ion one *m/z* unit lower. However, [metal^{I}L$_2$X − H]$^-$ ions have been noted in the mass spectra of bis(acetylacetonato)-metal(II) complexes [5].

$$\text{metal}^{\text{II}}\text{L}_2 + \text{X}\cdot \longrightarrow (\text{metal}^{\text{II}}\text{L}_2\text{X} - \text{H}) + \text{H}\cdot \tag{14}$$

$$(\text{metal}^{\text{II}}\text{L}_2\text{X} - \text{H}) + e^- \xrightarrow{\text{M}} [\text{metal}^{\text{I}}\text{L}_2\text{X} - \text{H}]^- \tag{15}$$

$$(\text{metal}^{\text{II}}\text{L}_2\text{X} - \text{H}) + [\text{X}]^- \xrightarrow{\text{M}} [\text{metal}^{\text{II}}\text{L}_2\text{X}_2 - \text{H}]^- \tag{16}$$

The CF$_2$Cl$_2$ and CF$_3$Br NCI mass spectra of the cobalt complex contain ions of the form, [metal^{II}L$_2$R]$^-$ and [metal^{III}L$_2$RX]$^-$, where R corresponds to

CF_2Cl in the CF_2Cl_2 mass spectra and CF_3 in the CF_3Br mass spectra. Formation of these ions is attributed to radical/molecule reactions involving $\cdot CF_2Cl$ or $\cdot CF_3$ radicals followed by ionization of the products. Several formation mechanisms for these halogenated methyl radicals have been noted previously [5]. Comparable adducts have been identified in the CF_2Cl_2 and CF_3Br NCI mass spectra of bis(acetylacetonato)cobalt(II) [5]. Also, similar alkyl adduct ions with $R = C_nH_{2n+1}$ have been observed in the methane NCI mass spectrum of $Co(dpm)_2$ and several other cobalt(II) complexes [7]. In line with the previous studies it is suggested that the $\cdot CF_2Cl$ and $\cdot CF_3$ radicals react with the cobalt complex by an oxidative-addition mechanism where the radical attaches directly to the metal to produce a molecule of the form, $\text{metal}^{III}L_2R$, involving probable five-coordinate geometry around the metal, reaction (17). This process is observed only with the cobalt complex because of the ease of oxidation of cobalt to the +3 formal oxidation state. Resonance electron capture by $\text{metal}^{III}L_2R$ produces $[\text{metal}^{II}L_2R]^-$ while ionization by nucleophilic halide addition yields $[\text{metal}^{III}L_2RX]^-$; reactions (18) and (19). These organometallic ions presumably have five- and six-coordinate geometries respectively around the metal. No evidence for reactions involving $\cdot NF_2$ radicals was identified in any of the NF_3 NCI mass spectra.

$$\text{metal}^{II}L_2 + R\cdot \longrightarrow \text{metal}^{III}L_2R \qquad (17)$$

$$\text{metal}^{III}L_2R + e^- \xrightarrow{M} [\text{metal}^{II}L_2R]^- \qquad (18)$$

$$\text{metal}^{III}L_2R + [X]^- \xrightarrow{M} [\text{metal}^{III}L_2RX]^- \qquad (19)$$

Cluster ions containing two metal atoms are a noteworthy feature of several of the mass spectra. These ions have the general form, $[\text{metal}^{II}{}_2L_yX_z]^-$ where $y + z = 5$, and are most prominent in the mass spectra of the zinc complex. The cluster ions were observed to be particularly abundant at high filament emission currents and high metal complex concentrations. These observations are consistent with the occurrence of ion/molecule clustering reactions in the NCI plasmas. Some possible clustering processes are shown in reactions (20)–(28). Significantly, the formation of several of these cluster ions, particularly $[\text{metal}^{II}{}_2X_5]^-$, provides some confirmation for the presence of $\text{metal}^{II}X_2$ molecules in the plasmas and therefore provides further evidence for the occurrence of reactions (8) and (11).

$$[\text{metal}^{II}L_2X]^- + \text{metal}^{II}L_2 \longrightarrow [\text{metal}^{II}{}_2L_4X]^- \qquad (20)$$

$$[\text{metal}^{II}L_2X]^- + \text{metal}^{II}LX \longrightarrow [\text{metal}^{II}{}_2L_3X_2]^- \qquad (21)$$

$$[\text{metal}^{II}L_2X]^- + \text{metal}^{II}X_2 \longrightarrow [\text{metal}^{II}{}_2L_2X_3]^- \qquad (22)$$

$$[\text{metal}^{II}LX_2]^- + \text{metal}^{II}L_2 \longrightarrow [\text{metal}^{II}{}_2L_3X_2]^- \qquad (23)$$

$$[\text{metal}^{II}LX_2]^- + \text{metal}^{II}LX \longrightarrow [\text{metal}^{II}{}_2L_2X_3]^- \qquad (24)$$

$$[\text{metal}^{II}LX_2]^- + \text{metal}^{II}X_2 \longrightarrow [\text{metal}^{II}{}_2LX_4]^- \qquad (25)$$

$$[\text{metal}^{II}X_3]^- + \text{metal}^{II}L_2 \longrightarrow [\text{metal}^{II}{}_2L_2X_3]^- \qquad (26)$$

$$[\text{metal}^{II}X_3]^- + \text{metal}^{II}LX \longrightarrow [\text{metal}^{II}{}_2LX_4]^- \qquad (27)$$

$$[\text{metal}^{II}X_3]^- + \text{metal}^{II}X_2 \longrightarrow [\text{metal}^{II}{}_2X_5]^- \qquad (28)$$

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