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Coordination Chemistry Reviews 250 (2006) 2325–2334
COORDINATION CHEMISTRY REVIEWS
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Review

Photochemistry of azide-moiety containing inorganic compounds

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Accepted 9 March 2006

Contents

Abstract

Results obtained to date document that inorganic compounds containing azide-moiety undergo several kinds of photochemical processes, the most extensively studied being (i) singlet or triplet six-electron nitrene ($-$N) intermediate formation at a dinitrogen molecule elimination from the azido ligand preserving the central atom oxidation state; (ii) transformation of azido ($-N_3$) to nitrido ($\equiv$N) complexes associated with a two-electron oxidation of the central atom; (iii) oxidation of azido anionic ligand (N_3^-) to its radical ($N_3^\bullet$) accompanied by a one-electron reduction of the central atom; (iv) non-redox photoejection of azido ligands from the coordination sphere or its substitution, usually for a solvent molecule; (v) photoisomerization reaction; (vi) reaction of other than azido ligand in the primary coordination sphere; (vii) reactions of azido group being peripheral part of organic ligands. Moreover, azido complexes are involved in pure photophysical deactivation processes without any chemical change. This contribution is aimed at reviewing all of the mentioned deactivations.

Keywords: Photochemistry; Azide complexes; Redox processes; Azidyl radical; Nitrene formation; Nitrido ligand

1. Introduction

Systems of free azides or azido-moiety containing compounds may, in principle, be grouped into four classes:

1. organic azido compounds (e.g. azidobenzene $C_6H_5N_3$);
2. inorganic compounds containing free (e.g. ionic salts such as NaN_3) and protonated (HN_3) azide anions;
3. coordination compounds with azido ligand(s) covalently bonded to the central atom (e.g. $[Co(NH_3)_5(N_3)]^{2+}$);
4. coordination compounds containing organic azido ligand(s) (e.g. azidoferrocene $[Fe(C_5H_5)(C_5H_4N_3)]$).

Members of each of the mentioned groups have been subjected to photochemical investigation and a wide variety of

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doi:10.1016/j.ccr.2006.03.004

photochemical processes has been unveiled. The photochemical behaviour of organic azides (class 1) lies usually outside the interest of the chemist engaged in inorganic or coordination chemistry. However, the knowledge obtained through investigation of organic azides may be very inspiring and helpful in the interpretation of behaviour of inorganic azido complexes and salts. This opinion can be exemplified by a transfer of information on nitrene intermediates – which is very deeply elaborated in the photochemistry of organic azides – to the realm of photochemistry of azido complexes. In spite of its stimulating impact to inorganic photochemistry, the area of photochemical behaviour of organic azides remains beyond the scope of this contribution and will not be covered in this paper. The reader may find necessary information elsewhere (see e.g. [1–4]).

Up to now, the photochemistry of inorganic azides or azido complexes has been focused mainly on unveiling the mechanisms of photophysical and photochemical deactivation processes, frequently stimulated by a vision of practical applications of the acquired knowledge. In this contribution this aspect is reviewed with a stress put on the photochemistry of iron(III) compounds.

Most of the fundamental results obtained before 1990 are described in comprehensive monographs [5,6] and reviews [7,8]. This contribution treats in particular, subsequent information, however, some older principal papers are also mentioned. Individual photophysical processes and photochemical reactions are tentatively classified based on the primary deactivation processes and/or their products.

2. Photophysical processes involving azide anions and azido complexes

Photophysical processes form an integral part of all deactivation processes of excited molecules. As typical examples, vibrational and rotational relaxation accompanying almost all chemical deactivations may be introduced. In this section, only systems with exclusively photophysical deactivation (i.e. without observable chemical change) are briefly mentioned. Of the known photophysical deactivations, mainly physical deactivation yielding the ground state reactants, intersystem crossing (*isc*) and energy transfer (*ent*) processes are typical of the systems containing free azide anions or excited azido complexes.

2.1. Photophysical processes of free azide anion

Free anion N_3^- behaves in its ground state as an efficient quencher of singlet dioxygen molecules $^1O_2$ in water, organic solvents and mixed aqueous–organic media. The rate constants of the quenching k_q ranging from $2.24 \times 10^8\,M^{-1}\,s^{-1}$ (ethanol–D_2O mixture) up to $2.8 \times 10^9\,M^{-1}\,s^{-1}$ (acetonitrile–D_2O mixture) were determined for several solvents and their mixtures [9,10]. Such constants are routinely used as standards to calculate k_q values for the $^1O_2$ quenching by various substrates. The measured values showed that the quenching rate constants in most mixtures cannot be reliably predicted using simple additivity rules estimating from the k_q values obtained for pure solvents. The activation energy for the $^1O_2$ quenching by azide in D_2O is $11.3\,kJ\,mol^{-1}$ [9]. With respect to the quenching mechanism, it is generally believed that the interaction proceeds through a partial charge transfer intermediate followed by its dissociation to ground state reactants without any chemical change [11]:

$$^1O_2 + N_3^- \rightarrow {}^3O_2 + N_3^- \tag{1}$$

In practical application only the anionic form N_3^- is able to effectively quench the $^1O_2$, HN_3 is almost inactive in this process.

2.2. Photophysical processes involving excited azido complexes

In connection with the photochemistry of the environment, photodynamic therapy and other attractive fields of human medicine, energy transfer processes generating $^1O_2$ or other active oxygen species have been extensively investigated. Simultaneously, azido complexes have been involved in research of industrial importance, mainly on the photooxidation of organic compounds by $^1O_2$ catalyzed by inorganic complexes.

Anbalagan [12] presents the results of the generation of the $^1O_2$ by energy transfer processes involving platinum(II) or palladium(II) complexes in their MLCT excited states. Among several other compounds, two azido complexes, $[Pt(dmbpy)(N_3)_2]$ and $[Pd(dmbpy)(N_3)_2]$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) dissolved in DMF were subjected to the study. Of all the complexes investigated, the excited $[Pt(dmbpy)(N_3)_2]$ was most effective in $^1O_2$ production. The suggested mechanism of formation of $^1O_2$ consists of three steps (GS = the singlet ground state of the complex, left superscripts denote the multiplicity of molecules):

$$_{GS}[Pt(dmbpy)(N_3)_2] \xrightarrow{h\nu} {}^1[Pt(dmbpy)(N_3)_2] \tag{2}$$

$$^1[Pt(dmbpy)(N_3)_2] \xrightarrow{isc} {}^3[Pt(dmbpy)(N_3)_2] \tag{3}$$

$$^3[Pt(dmbpy)(N_3)_2] + {}^3O_2 \xrightarrow{ent} {}_{GS}[Pt(dmbpy)(N_3)_2] + {}^1O_2 \tag{4}$$

The generated $^1O_2$ subsequently acts as an oxidizing agent towards industrial organic substances. The author did not mention any photochemical changes in platinum or palladium complexes within the study. From the formal point of view, the generation of $^1O_2$ can be taken as the opposite process to its quenching, which is a typical property of free azide anion [9,10].

3. Photochemical processes of inorganic azides and azido complexes

3.1. Free and protonated azide anion, and azide salts

Free anion N_3^- or hydroazoic acid HN_3 are involved predominantly in two kinds of photochemical and/or photophysical processes: the previously mentioned quenching of $^1O_2$, and the generation of the nitrene anion N^-.

Within the development of photochemistry and of quantification of the efficiency of photochemical processes, a significant role played by gaseous HN_3 was investigated by Beckman [13–15]. In addition to his measurement of the quantum yield of HN_3 photodecomposition, he proposed a mechanism stating that the primary photochemical step was conversion of HN_3 to the highly reactive HN and molecular nitrogen N_2.

Free anion N_3^- is photochemically active when irradiated by UV radiation below 270 nm (its absorption threshold is to some extent modified by the solvent used). The population of intraligand IL or charge transfer to solvent CTTS excited states by a photon absorption leads to anion decomposition forming N_2 (which was identified) and probably a highly reactive six-electron anionic N^- as an intermediate (its formation was suspected based on final reaction products [16,17]). The formation of such an intermediate was also postulated in [18–21] where with 254 nm irradiation of a methanolic solution of NaN_3, formaldehyde, CH_2O, was identified as a reaction product of N^- with methanol molecules. In this case, the absorbed photons populated an intraligand singlet $^1N_3^-(n \rightarrow \pi^*)$ excited state. From this state, deactivation in the form of decomposition to N_2 and N^- occurs:

$$_{IL}{}^1N_3{}^- \rightarrow N_2 + N^- \tag{5}$$

The electronically unsaturated anion N^- is a very strong two-electron oxidant able to react with surrounding molecules through electron and/or atom abstraction. In methanolic media it reacted producing formaldehyde obeying the stoichiometry:

$$N^- + 2CH_3OH \rightarrow CH_2O + NH_3 + CH_3O^- \tag{6}$$

The integral quantum yield of CH_2O formation was calculated based on the determined rate of CH_2O formation and approached a value of $\Phi \cong 1 \times 10^{-2}$. In the presence of iron(III) complexes, irradiation by radiation absorbed both by the complexes and free or coordinated azide anions causes the simultaneous photoreduction of iron(III) to iron(II) and generation of N^- anions behaving as oxidant towards formed iron(II). The consequence is that the overall quantum yield of iron(II) formation is significantly lower when using UV radiation than that when applying visible incident light and the wavelength dependence of the quantum yield of iron(II) formation has a “bell-like” shape [20,21].

The photochemical investigation of “pure” simple inorganic azides is very rare. The reason is obvious and follows from the fact that the majority of photochemical studies are performed in solutions in which both a partial dissociation of the salts and bonding of solvent molecules to the central atom occur forming thus photochemically active complexes. In fact, the authors of only one paper [22] declared that it dealt with a simple salt. Irradiation of $Ga(N_3)_3$ in acetonitrile leads to a reductive elimination of N_2:

$$Ga(N_3)_3 \xrightarrow{h\nu(LMCT)} Ga(N_3) + 3N_2 \tag{7}$$

The primary product of the oxidation is probably the radical $N_3^\bullet$, not a nitrene. The authors suppose the presence of undissociated but solvated salt $Ga(N_3)_3(CH_3CN)$ in the solution investigated. The product of the photochemical decomposition – the soluble luminescent $Ga(N_3)$ – differs from insoluble gallium(III) nitride, GaN obtained by thermal decomposition of the parent salt. The result complies with a general rule stating that azido compounds of metals with s^0 electron configuration undergo photochemical reductive elimination leading to the corresponding s^2 compounds [22].

For the sake of completeness we include here information on oxidation properties of the azide radical $N_3^\bullet$ which reacts in aqueous solutions with hydrated Fe^{2+} ions, with the second-order rate constant of $(3.2 \pm 1.0) \times 10^6\,M^{-1}\,s^{-1}$ [23]. The immediate product is a novel radical $(Fe^{2+}\cdot N_3^\bullet)_{aq}$ having a characteristic absorption at 300 and 410 nm ($\varepsilon = 1700$ and $1100\,M^{-1}\,cm^{-1}$, respectively). This radical undergoes an intramolecular electron transfer forming hydrated azido iron(III) complex with the first-order rate constant of $(1.2 \pm 0.3) \times 10^4\,s^{-1}$. These data are of significant value in the interpretation of the back electron transfer between the primary products of the photoredox decomposition of azido complexes, when one of the products is the radical $N_3^\bullet$.

A very peculiar significance of radical $N_3^\bullet$ formation has been found in cosmology. The radical $N_3^\bullet$ acts as a discriminator between ion-irradiated and UV-photolyzed astronomical ices. Irradiation of N_2 with 600 keV electrons [24] and solid N_2 or N_2-rich ices [25] with 0.8 MeV protons produces $N_3^\bullet$ radicals. In contrast, no such generation was observed when solid N_2 and N_2-rich ices were first photolyzed by far-UV photons. This difference could be used to identify ion-radiated ices in interstellar grains and in the outer solar system. Moreover, the radical $N_3^\bullet$ might be used as a tracer of solid-phase interstellar N_2 which is difficult to observe directly [25].

3.2. Photochemical reactions of azido complexes

Comparing with the photoredox chemistry of structurally similar halogeno complexes, two specific features relate to azido complexes. The first one lies in the very peculiar and rich photoreactivity of azido ligands, the other concerns the shape of wavelength dependence of the quantum yield, Φ/λ_{irr} of the central atom involved processes. In contrast to the halogenides, the ability of the azide anion to undergo intraligand decomposition opens the possibility of finding a “bell-like” Φ/λ_{irr} dependence.

Azido ligands can be converted in the primary photochemical step to a six-electron triplet or singlet nitrene intermediate (Section 3.2.1), a nitrido ligand coordinated to the central atom by a triple bond (Section 3.2.2), or an azidyl radical $N_3^\bullet$ (Section 3.2.3). In some cases the absorption of a photon can result in the photoejection of azido ligand from the primary coordination sphere and its possible substitution, usually for a solvent molecule or in photoisomerization (Section 3.2.4). Chemical deactivations not involving azido ligand were also observed (Section 3.2.5). Photochemical reactions of azido group containing organic ligands are mentioned in Section 3.2.6.

In the general expression of individual photoprocesses, the composition of the complexes will be, for the sake of simplicity, described as $[(L)_xM^n{-}N_3]$ (L_x are the other ligands, n is the oxidation number of the central atom).

3.2.1. Nitrene intermediate formation

In spite of the experimental possibilities offered by pico or femtosecond spectroscopic methods, direct experimental observation of the nitrene intermediate:

$$[(L_x)M^n - N]$$

with a single M–N bond has not yet been achieved. Based predominantly on identification of final products and on knowledge obtained in organic photochemistry [1–4]; however, it is generally accepted that such an intermediate:

$$[(L)_x M^n\text{–}N_3] \xrightarrow{h\nu} [(L_x)M^n\text{–}N] + N_2 \qquad (8)$$

is involved in the mechanism of several photoinduced processes. As a classical example, the conversion of $[Ir(NH_3)_5)N_3)]^{2+}$ to the chloramine complex $[Ir(NH_3)_5)(NH_2Cl)]^{+}$ known for more than 40 years, is believed to involve the nitrene $[Ir(NH_3)_5)(N)]^{2+}$ and/or the imido $[Ir(NH_3)_5)(NH)]^{3+}$ intermediates [26].

$$[Ir(NH_3)_5)N_3)]^{2+} \xrightarrow{h\nu(\text{IL or LMCT})} [Ir(NH_3)_5)N)]^{2+} + N_2 \qquad (9)$$

$$[Ir(NH_3)_5)N)]^{2+} + H^+ \rightarrow [Ir(NH_3)_5)(NH)]^{3+} \qquad (10)$$

$$[Ir(NH_3)_5)(NH)]^{3+} + H^+ + Cl^- \rightarrow [Ir(NH_3)_5)(NH_2Cl)]^{3+} \qquad (11)$$

Analogous steps were proposed for photochemical behaviour of rhodium(III) azido complexes [27].

The issue of nitrene formation, whether of singlet or triplet nature, deserves more detail rationalization. Whereas the two nitrenes are structurally identical, their chemical behaviour is vastly different. The ground state of nitrene is a triplet. The triplet nitrene is a diradical, relatively unreactive towards Lewis bases but effective in abstraction and insertion reactions. The singlet nitrene with one empty orbital is a very strong Lewis acid. In their original reports [26,27], Basolo and co-workers proposed that nitrene formation is favoured for metals not having a stable one lower oxidation number and for metals having filled d-orbitals that can back-donate into the vacant nitrogen orbitals of the nitrene stabilizing thus the metal–nitrene moiety. Basolo postulated nitrene formation based on the identification of the final product $[Ir(NH_3)_5)(NH_2Cl)]^{+}$ and its rhodium analogue. Nitrene intermediates were postulated also for seemingly redox stable complexes such those of nickel(II) with two mono or one bidentate phosphine ligand(s) and two coordinated azido ligands, abbreviated as $[NiP_2(N_3)_2]$, where P_2 is two mono- or one diphosphine ligand. Theoretical [28] and experimental [29,30] studies of photochemical decomposition processes occurring in irradiated solutions of the complexes above showed that a postulated intermediate $[NiP_2(N)(N_3)_2]$ may undergo an intramolecular coupling reaction forming nickela-tetrazoles $[NiP_2(N_4)]$ with a chelating $(N{=}N{-}N{=}N)^{2-}$ ligand. However, in spite of great effort and the application of several time-resolved methods, the intermediate was not directly unambiguously identified. The complexes $[NiP_2(N_3)_2]$ were potentially useful in photocatalyzed cyclotrimerization of acetylene to benzene, with the highest efficiency determined [31] for $[Ni(dppe)(N_3)_2]$.

Irradiation of the complex *trans*-$[Ni(PEt_3)_2(N_3)_2]$ in the solid state at various temperatures led, however, to different products than that obtained in solution. When irradiating the complex within the d–d bands, formation of ion-paired $[Ni(PEt_3)_2(N_3)]^+N_3{}^-$ occurred. However, when populating higher energy LMCT states, there was primary ejection of a single PEt_3 ligand generating a three-coordinate Ni(II) complex, followed by an associative reaction to form the isolable azido-bridged dimer $[(PEt_3)(N_3)Ni(\mu\text{-}N_3)_2Ni(N_3)(PEt_3)]$. In this case no nitrene formation was considered [32].

Based on the molecular and crystal structures of the photochemically produced diamagnetic trimer $[\{Ni(PMe_3)Cl\}_3(\mu_3\text{-}NPMe_3)(\mu_3\text{-}NH)]$ with phosphorane-imido and imido ligands in capping positions or the tetrameric $[(NiCl)_4(\mu_2\text{-}NPMe_3)_4]$, the formation of a singlet nitrene intermediate $[NiCl(N)(PMe_3)_2]$ from the excited $[NiCl(N_3)(PMe_3)_2]$ was proposed [33]. Also in this work, nitrene means, in fact, rather imido bridging ligand.

Further information on the nitrene comes from investigation of two iridium(III) azido dithiocarbamato complexes. Insertion of a nitrogen atom as a product of azide ligand photodecomposition at $T = -30\,°C$ in the complex $[(\eta^5\text{-}C_5Me_5)Ir^{III}(R_2dtc)(N_3)]$, where R = Me or Et [34] into an Ir–S bond gives rise to a novel bidentate ligand $NSC(NR_2)S^{2-}$ of nearly planar structure forming with the central atom a five-membered chelate ring. The new Ir–N bond is of double-bond character.

A simple and elegant method of synthetic perspective was described by Hennig et al. [29,30] who irradiated azido complexes in the presence of CO or CS_2 and was able to convert the $N_3{}^-$ anion to NCO^- or NCS^- anions, respectively.

Application of some recently developed experimental techniques, mainly of electrospray ionization [35] has revealed new horizons in the analysis and fundamental gas-phase ion investigation of coordination compounds, including azido complexes and nitrene-containing intermediates [36]. Specifically, the existence of the cation $[Pt(dien)N]^+$ formed under collision-induced dissociation in the gas phase from the starting $[Pt(dien)N_3]^+$ was demonstrated using a modified quadrupole ion-mass spectrometry. Its structure was evaluated and reactivity studied via ion–molecule reactions method using several isotopically labelled analogues of the starting complex. The cation $[Pt(dien)N]^+$ was not formed photochemically in the study, which, however, does not matter. A very detailed study revealed that the cation should, in fact, be described neither as a complex with the six-electron single-bonded nitrene nor as triple-bonded nitrido complex, but rather as an intermediate with a double-bonded imine NH-moiety coordinated to the central tom Pt^{IV}, the hydrogen atoms originating from the diene ligand. This observation supports the presumption of the strong atom-abstracting ability of the triplet nitrenes. The intermediate decomposed releasing ammonia molecules.

Very fast (femtosecond) spectroscopic techniques are needed to obtain unambiguous evidence for nitrene formation, and for its spin state and nature, as well as to distinguish between nitrene and imido ligands.

3.2.2. Nitrido complexes formation

Photoredox generation of nitrido complexes by the denitrogenation of corresponding azido complexes can, in general, be expressed as:

$$[(\mathrm{L})_x\mathrm{M}^n\text{–}\mathrm{N}_3]\xrightarrow{h\nu(\mathrm{IL})}[(\mathrm{L})_x\mathrm{M}^{n+2}\equiv\mathrm{N}]+\mathrm{N}_2 \qquad (12)$$

Since the nitride anion N^{3-} is one of the strongest π-donor ligands, a necessary prerequisite for the formation of stable nitride species is the availability of suitable empty d-orbitals of the central atom. Thus, the vanadium(V), chromium(V), manganese(V) and even iron(V) central atoms should be ideally suited for the formation of nitrido complexes. Due to the enormous trans-influence of the nitrido ligand, a (potential) ligand bonded in a trans-position is labilized to such an extent that it is not able to coordinate and the majority of nitrido complexes are thus five-coordinate, square-pyramidal with the nitrido ligand in the apical position.

Results obtained so far, have shown that the photochemically produced nitrido complexes can be grouped into four main families, namely:

(i) mononuclear complexes with unusually high oxidation number of the central atom,
(ii) dinuclear complexes with different oxidation numbers and/or spin states of the central atoms linked via a bridging nitrido ligand,
(iii) dinuclear complexes with identical oxidation number of the central atoms connected by a bridging nitrido ligand,
(iv) polymeric complexes with bridging nitrido ligands.

As documented by several experiments, a mode of photoredox reactivity of some complexes may be tuned by variation of the experimental conditions and the structure of the complexes investigated. Not infrequently the irradiation of one complex may also lead, along with nitrido complexes, to other products.

Iron(III) azido complexes with chelating or macrocyclic ligands can serve as an instructive example. Photolysis of macrocyclic complexes with porphinato(2−) (por), phthalocyaninato(2−) (Pc) or 1,4,8,11-tetraazacyclotetradecane (cyclam) ligands at room temperature usually leads to the photoreduction of the iron(III) central atom to iron(II) accompanied by oxidation of azido ligands to its radical (Section 3.2.3).

Irradiation of thin solid films of $[\mathrm{Fe(por)(N_3)}]$ at 30 K [37], *trans*-$[\mathrm{Fe(cyclam)(N_3)_2}]$ [38] or $[\mathrm{Fe(cyclam\text{-}acetato)(N_3)](PF_6)}$ [39] in frozen acetonitrile solutions at 77 K, yields in the primary processes, mononuclear nitrido iron(V) complexes with an Fe≡N triple-bond, i.e. [Fe(por)(N)], $[\mathrm{Fe(cyclam)(N_3)(N)}]$ and $[\mathrm{Fe(cyclam\text{-}acetato)(N)](PF_6)}$, respectively. The products remain stable only at the given low temperatures.

Photochemical formation of the catalytically active nitrido iron(V) species from the potent precursor *trans*-$[\mathrm{Fe(cyclam)(N_3)_2}]^+$@NaY encapsulated in zeolite-Y was envisaged in paper [40]. The authors believed that the encapsulation of the azido complexes within the zeolite supercages could restore the highly reactive mononuclear nitrido iron(V) species preventing the formation of dinuclear molecules even at ambient temperature.

The photochemical behaviour of cyclam-containing complexes depends, along with the temperature, also on their stereochemistry [38]. Photolysis of the low-spin *trans*-$[\mathrm{Fe(cyclam)(N_3)_2}]^+$ in MeCN at temperatures of −35 and 20 °C leads to the dinuclear mixed-valence complex $[\{trans\text{-}(\mathrm{cyclam})\mathrm{Fe^{III}(N_3)}\}(\mu\text{-N})\{trans\text{-}\mathrm{Fe^{IV}(cyclam)(N_3)}\}]^{2+}$ with localized antiferromagnetically coupled intermediate-spin iron(III) ($S = 3/2$) and low-spin iron(IV) ($S = 1$). On the other hand, photolysis of the high-spin *cis*-$[\mathrm{Fe(cyclam)(N_3)_2}]^+$ in MeCN at −35 °C gives rise to a $[\{cis\text{-}(\mathrm{cyclam})\mathrm{Fe^{III}(N_3)}\}(\mu\text{-N})\{trans\text{-}\mathrm{Fe^{IV}(cyclam)(N_3)}\}]^{2+}$ with localized antiferromagnetically coupled high-spin iron(III) ($S = 5/2$) and low-spin iron(IV) ($S = 1$).

A similar difference was also documented in both iron central atoms for the dinuclear $[\{\mathrm{L(Cl_4\text{-}cat)Fe^{III}}\}(\mu\text{-N})\{\mathrm{Fe^{IV}(Cl_4cat)L}\}]$, $[\{\mathrm{L(Ph_2acac)Fe^{III}}\}(\mu\text{-N})\{\mathrm{Fe^{IV}(Cl_4cat)L}\}]$, and $[\{\mathrm{L(nadiol)Fe^{III}}\}(\mu\text{-N})\{\mathrm{Fe^{IV}(nadiol)L}\}]$, formed upon irradiation of the corresponding mononuclear azido iron(III) complexes, where L represents tridentate 1,4,7-trimethyl-1,4,7-triazacyclononane, $\mathrm{Cl_4}$cat is the tetrachlorocatecholate(2−), $\mathrm{Ph_2}$acac is the 1,3-diphenylpropane-1,3-dionate(1−), nadiol is naphthaline-2,3-dionate(2−) [41].

The results obtained using complexes with a flexible coordination sphere differ from those found when photolyzing structurally more rigid porphinato or phthalocyaninato azido iron(III) complexes. In the latter case both iron atoms in dinuclear complexes are equivalent with the valence delocalization in the linear $\{\mathrm{Fe^{3.5}{=}N{=}Fe^{3.5}}\}$ core [42]. Such delocalization seems to be a general phenomenon for porphinato and phthalocyaninato complexes and was even found in cases with two different macrocyclic ligands, such as in $[\mathrm{(TPP)Fe^{3.5}}(\mu\text{-N})\mathrm{Fe^{3.5}(Pc)}]$, where TPP is tetraphenylporphyrinato(2−) ligand [43].

Detailed investigation indicated that the (μ-nitrido)diiron products were formed by the combination of iron(II) and iron(V) generated concurrently via photoreduction and photooxidation of the parent iron(III) azido complexes, respectively (charges of the complexes are omitted):

$$[(\mathrm{L}_x)\mathrm{Fe^{II}}] + [(\mathrm{L}_y)\mathrm{Fe^{V}}{\equiv}\mathrm{N}] \rightarrow [(\mathrm{L}_x)\mathrm{Fe^{III}}(\mu\text{-N})\mathrm{Fe^{IV}}(\mathrm{L}_y)]\,or\; [(\mathrm{L}_x)\mathrm{Fe^{3.5}}(\mu\text{-N})\mathrm{Fe^{3.5}}(\mathrm{L}_y)] \qquad (13)$$

The formation of a mononuclear porphinatoiron(V) nitrido intermediate was proven by Nakamoto [37], and the production of porphinatoiron(II) associated with radical $N_3^{\bullet}$ releasing from the coordination sphere was demonstrated by spin trapping EPR [44].

Besides reaction (13), alternative mechanisms, summarized in a review [45], were proposed for the formation of dinuclear nitrido-bridged complexes. One of them described iron(II) complex generation as the following process:

$$[\mathrm{Fe^{V}(por)(N)}] + [\mathrm{Fe^{III}(por)(N_3)}] \rightarrow 2[\mathrm{Fe^{II}(por)}] + 2\mathrm{N_2} \qquad (14)$$

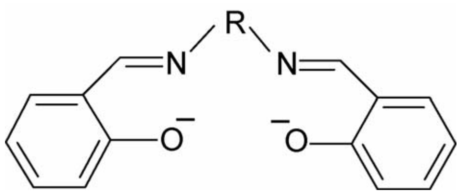

Fig. 1. Schematic structure of salen-type N_2O_2-ligands. $R = C_2H_4$, N_2O_2 = salen; $R = C_3H_6$, N_2O_2 = salpn; $R = C_6H_4$, N_2O_2 = salph; $R = C_6H_{10}$, N_2O_2 = salchd.

another suggested that iron(V) species were products of a back reaction of the radical $N_3^{\bullet}$, and [Fe^{II}(por)] produced by the following reaction:

$$N_3^{\bullet} + [Fe^{II}(por)] \rightarrow [Fe^{V}(por)(N)] + N_2 \qquad (15)$$

A priori, none of the mechanisms may be excluded and it might happen that several of them are realized simultaneously in irradiated systems with the proportion depending on experimental conditions and the complex composition.

Along with iron(V) nitride complexes, attention has also been devoted to nitrido complexes of chromium(V) and manganese(V), in all known cases with tetradentate equatorial ligands of porphinato, cyclam or Schiff bases, or with chelating tridentate and bidentate ligands. Similarly as in case of iron(V) nitrides, porphinato(2−) [46,47] and phthalocyaninato(2−) [48] manganese(V) nitrido complexes were prepared first, followed some years later by Schiff base containing species [49,50].

Depending on solvents used and temperatures applied, the irradiated complexes [Cr^{III}(por)(N_3)] and [por)(N_3)] can be quantitatively transformed to fairly stable [Cr^{V}(por)(N)] and [Mn^{V}(por)(N)], respectively, for a variety of porphyrins [45]. As an example of the solvent dependence [Mn^{III}(por)(N_3)], is transformed to manganese(V) nitrides in benzene or toluene and in methyltetrahydrofuran (MeTHF) at −80 °C, but [Mn^{II}(por)] is formed in MeTHF at room temperature.

Laser flash photolysis of the pentacoordinate [Cr^{III}(salchd)(N_3)] and [Mn^{III}(salchd)(N_3)] performed in acetonitrile solution (where Schiff base N_2O_2-ligand salchd = *N*,*N*′-cyclohexane-1,2-bis(salicylideneiminato)(2−), Fig. 1) revealed the involvement of two intermediates in the photoredox processes. Photodenitrogenation of [Cr^{III}(salchd)(N_3)] occurring through the intermediacy of a triplet chromium(II) nitrene absorbing at 420 nm yields the mononuclear complex [Cr^{V}(salchd)(N)] [51]. The second transient characterized by the 470 nm band was assigned to [Cr^{II}(salchd)].

Polymeric [Cr(salpn)(N)] (where H_2salpn = *N*,*N*′-propane-1,3-bis(salicylideneimonato)(2−), Fig. 1) was prepared by irradiation of an acetonitrile solution of [Cr(salpn)(N_3)] [52]. An analogous complex, [Cr(naphprn)(N)], (naphprn = *N*,*N*′-trimethylene-bis(naphthylideneiminato)(2−)), appeared upon irradiation of [Cr(naphprn)(H_2O)(N_3)] in DMF [53]. In both cases identification of chromium(V) and Cr≡N was based on EPR and IR (or Raman) spectra using ^{15}N azides.

A polymeric nitrido complex, [Mn^{V}(salpn)(N)] with a linear Mn≡N·Mn≡N chain structure is formed by photolysis of [Mn^{III}(salpn)(N_3)] in acetonitrile [54]. It is interesting that upon recrystallization from methanol the five coordinate monomeric [Mn^{III}(salpn)(N_3)]·CH_3OH, is produced probably due to the trans-effect of the azido ligand.

In the context of investigations concerning industrially relevant reactions involving nitrogen atom transfer to olefins, attention has been paid to the photochemical conversion of [Cr^{III}(N_2O_2)(N_3)] and [Mn^{III}(N_2O_2)(N_3)] azido complexes to mononuclear [Cr^{V}(N_2O_2)(N)] and [Mn^{V}(N_2O_2)(N)] nitrides, where the Schiff base N_2O_2-ligands are salen or salph (*N*,*N*′-phenylene-1,3-bis(salicylideneiminato)(2−), Fig. 1). In connection with the known catalytic potential of zeolites and their ability to enhance the emission efficiency of immobilized hosts, the conversion was also followed inside the zeolite-Y supercages [55]. Based on room-temperature emission of the supported azides the authors concluded that the denitrification process of azide-to-nitride conversion takes place through an adiabatic crossing from the excited azido complex to the excited nitrido complex. Comparing the results obtained within the study of iron(III) azides [40] with those given in [55] it follows that what was anticipated for iron compounds was achieved with chromium and manganese compounds.

Along with five-coordination of the central atom, some octahedral nitrido complexes of the general formula [M^{V}(L_3)(L_2)(N)] were also quantitatively prepared via photolysis of the corresponding [M^{III}(L_3)(L_2)(N_3)] in the solid state or in solutions [56]. In the formulae, M = Cr or Mn; L_3 = the tridentate macrocyclic 1,4,7-triazacyclononane or its *N*-methylated derivative; the bidentate ligands L_2 are pentane-2,4-dionate(1−), 2,2,6,6-tetramethylheptane-3,5-dionate(1−), picolinate(1−), phenanthroline or oxalate(2−) (ox). The generated positive charge of the complexes was balanced with ClO_4^- or $[PF_6]^-$ anions. In addition to the mononuclear products, the nitrido-bridged mixed-valence compound [(L_3)(ox)Cr^{III}(μ-N)Cr^{V}(ox)(L_3)]N_3 was prepared irradiating the complex [Cr(L_3)(ox)(N_3)] in the solid state.

In dinuclear nitrido complexes discussed until now, the role of the bridge was played by the nitrido ligand. Under certain experimental conditions, however, azido-bridged nitrido complexes can also be synthesized. Thus, irradiation of *trans*-[Mn^{III}(cyclam)(N_3)$_2$]ClO_4 in methanol at −35 °C with 350 nm radiation led to the isolable product [{*trans*-[(cyclam)Mn^{V}(N)]}(μ-N_3)](ClO_4)$_3$ [57]. Products of irradiation of [(L_3)Mn^{III}(N_3)$_3$] (L_3 = 1,4,7-triazacyclononane) in MeCN depend on the temperature and wavelength. At room temperature using 254 nm radiation the bridged [{(L_3)Mn^{II}(N_3)}(μ-N_3)$_2$] is formed, at −35 °C and 350 nm radiation the mononuclear [(L_3)Mn^{V}(N)(N_3)$_2$] is produced.

3.2.3. *Azidyl radical formation*

Azidyl radical $N_3^{\bullet}$ formation is associated with a one-electron reduction of the central atom conditioned by a LMCT excited state population. The general expression of the homolytic cleavage of the M^n–N_3 bond is as follows:

$$[(L)_xM^n\text{–}N_3] \xrightarrow{h\nu(\text{LMCT})} [(L)_xM^{n-1}] + N_3^{\bullet} \qquad (16)$$

Depending on the central atom redox stability in the product $[(L)_xM^{n-1}]$ formed, it may preserve itself as a redox stable complex or it can undergo consecutive dark redox processes involving the central atom. The threshold energy for homolytic dissociation of the $M^n–N_3$ bond is of a similar value (259 kJ mol^{-1}) to that of $M^n–NO_2$ (248 kJ mol^{-1}) or $M^n–Br$ bonds (260 kJ mol^{-1}) for M = Co(III) [58].

The radical $N_3^\bullet$ has usually been identified by the EPR spin trapping method [31,59–62], mainly using the spin traps phenyl-*N*-*tert*-butylnitrone (PBN) or nitrosodurene (ND). Following Rehorek's pioneering work [29] providing the first direct EPR evidence of the radical $N_3^\bullet$ generated upon photolysis of aqueous or methanolic solutions of $[Co^{III}(NH_3)_5(N_3)]^{2+}$ and $[Co^{III}(CN)_5(N_3)]^{3-}$, EPR spin trapping has been successfully applied in the radical $N_3^\bullet$ identification, e.g. in irradiated systems containing porphyrinato complexes $[Mo^VO(por)(N_3)]$ or $[Fe^{III}(por)(N_3)]$ [44,62], $[Pt^{II}(N_3)_2(PPh_3)_2]$ and $[Pd^{II}(N_3)_2(PPh_3)_2]$ [31,63–65], Fe^{III}(*cyt*)(N_3), where Fe^{III}(*cyt*) is ferric cytochrome *c* [64,66], Vitamin B_{12} model complexes $[LCo^{III}(chel)(N_3)]$, where chel are various bidentate or tetradentate chelating ligands and L are monodentate ligands [59], $[Au^{III}(N_3)_4]^-$ [67], etc.

Azidyl radicals are known to decompose in thermal secondary steps to nitrogen atoms and dinitrogen molecules. The nitrogen atom was identified at low temperatures through its EPR signal, e.g. in the photolyzed samples of $[Pt(CN)_4(N_3)_2]^{2-}$ [68], $[Sn(N_3)_6]^{2-}$ and $[Pb(N_3)_6]^{2-}$ [69,70]. In the cases of the photolysis of $[Sn(N_3)_6]^{2-}$ and $[Pb(N_3)_6]^{2-}$ in an ethanol/CH_2Cl_2 low-temperature matrix, no trace of paramagnetic Sn(III) or Pb(III) was identified and this fact was taken as an indication of simultaneous two-electron reduction of the central atoms.

The final product of the radical $N_3^\bullet$ decomposition is N_2 [69]. In several papers, there was no attempt to search for the radical $N_3^\bullet$, and its involvement in the mechanism is tacitly considered just based on the formation of nitrogen molecules or on the reduction of the central atom [71–73]. As examples of such work, reductive elimination of nitrogen from $[Pt(N_3)_6]^{2-}$ [68], photoreduction of Eu(III) to Eu(II) upon photolysis of aqueous europium(III) azido complexes [74], generation of platinum(0) species upon irradiation of thin solid amorphous films of platinum(II) azides on Si(1 1 1) [75] have useful applications as documented for nickel(II) azido complexes with various phosphines. Nickel(0) species generated with nitrogen elimination in DMSO catalyze the cyclotrimerization of acetylene with promising high yields and turnover numbers [31]. Analogous palladium(II) and platinum(II) complexes are catalytically inactive. In some cases the elimination of N_2 is accompanied by the elimination of azide anion N_3^-, such as in cases of $[Pt(N_3)_4]^{2-}$, $[Au(N_3)_2]^-$ or $[Hg(N_3)_3]^-$ [68], e.g.

$$[Hg(N_3)_3]^- \xrightarrow{h\nu(LMCT)} Hg + N_3^- + 3N_2 \qquad (17)$$

Two azido complexes, namely *cis*,*trans*-$[Pt^{IV}(en)(N_3)_2(OH)_2]$ and *cis*,*trans*-$[Pt^{IV}(N_3)_2(OH)_2(NH_3)_2]$ were studied as possible photochemotherapeutic agents both in the presence and in the absence of d(GpG) which is the reactive site towards cisplatin (d(GpG) = sodium salt of 2′-deoxyguanylyl(3′ → 5′)-2′(deoxyguanosine) [76]. Irradiation of the former complex in the absence of d(GpG) led to the reactive *trans*-$[Pt^{II}(en)(NH_2)(H_2O)]^+$ which has, as typical for aqua platinum(II) complexes, a high affinity to strong nitrogen donors such as d(GpG).

Irradiation of both these azido platinum(IV) complexes in the presence of d(GpG) gave rise to $[Pt^{II}(en)\{d(G^1pG^2)\text{-}N7^1,N7^2\}]^{2+}$ and *trans*-$[Pt^{II}(NH_3)_2\{d(G^1pG^2)\text{-}N7^1,N7^2\}]^{2+}$, respectively. The authors did not search for the fate of the azido ligands; it followed from the results, however, that both azido ligands were oxidized in the primary process to $N_3^\bullet$ radicals.

Elimination of azido ligands from excited complexes in the form of N_2 may give rise to highly reactive intermediates reacting by both intramolecular or intermolecular paths. In this sense, the complexes $[Ir(Cp)L(N_3)_2]$ (L = PMe_3, PPh_3, PCy_3; Cp = $C_5Me_5^-$) were subjected to a detail investigation [77], the complex $[Ir(Cp)(N_3)_2(PPh_3)]$ may serve as an example. Upon its irradiation in benzene (formally PhH), mixtures of $[Ir(Cp)(H)(Ph)(PPh_3)]$ formed by intermolecular reaction with benzene, and the orthometalated product $[Ir(Cp)(H)\{(\mu\text{-}Ph)PPh_2\}(PPh_3)]$ formed by intramolecular hydrogen-transfer reaction are produced. In several halogenated solvents (CCl_4, CH_2Cl_2 or $CHCl_3$) a chain of redox processes initiated by the primary photochemical elimination of N_2 results in the formation of chloro complexes, e.g. $[Ir(Cp)Cl_2(PPh_3)]$ from $[Ir(Cp)(N_3)_2(PPh_3)]$. From the viewpoint of stoichiometry, the reaction represents non-redox substitution of azido ligands for chloro ligands.

Reactions of a coordinatively unsaturated metal-containing radical formed upon elimination of $N_3^\bullet$, was also observed [63] during investigation of the photochemical behaviour of $[Pt^{II}(PPh_3)_2(N_3)_2]$. The metal localized radical $[Pt^I(PPh_3)_2(N_3)]$ abstracted a chlorine atom from the solvent CH_2Cl_2 forming $[Pt^{II}Cl(PPh_3)_2(N_3)]$. Thus, in a similar fashion to the iridium(III) complexes above [77], virtual non-redox photosubstitution of azido ligand for chloro ligand is, in fact, a result of some subsequently occurring redox processes.

3.2.4. Non-redox photoeliminations, photosubstitutions and photoisomerizations

In addition to photoredox processes, azido complexes may undergo photosubstitution reactions in which the azido ligand is substituted, e.g. for a solvent molecule, solv, in general:

$$[L_xM^{n+}–N_3] + solv \xrightarrow{h\nu(LF)} [L_xM^{n+}–solv] + N_3^- \qquad (18)$$

or it can be just ejected from the primary coordination sphere. While the former process is obviously of non-redox nature, the photoelimination is usually part of more complicated simultaneously occurring decomposition process. This involves formation of the $N_3^\bullet$ radicals transformed into nitrogen molecules as a final product and associated with central atom reduction. Several examples of azide ligand non-redox photoelimination are offered in [68,78], decomposition of $[Pt^{II}(N_3)_4]^{2-}$ and $[Au^I(N_3)_2]^-$ may serve as illustrative examples:

$$[Pt^{II}(N_3)_4]^{2-} \xrightarrow{h\nu(LMCT)} Pt^0 + 3N_2 + 2N_3^- \qquad (19)$$

$$2[\mathrm{Au^I(N_3)_2}]^- \xrightarrow{h\nu(\mathrm{LMCT})} 2\mathrm{Au^0} + 3\mathrm{N_2} + 2\mathrm{N_3^-} \quad (20)$$

Upon irradiation of $[\mathrm{Au^I(N_3)_2}]^-$ in acetonitrile MeCN, 70% of the reactant is transformed to colloidal gold while the residual 30% is converted to the complex $[\mathrm{Au^I(CN)_2}]^-$ [78] probably through abstracting the cyano groups from acetonitrile molecules by the photochemically generated gold atoms. Owing to the high reactivity of atomic gold (e.g. $E^\mathrm{o}(\mathrm{Au^+/Au}$ (atomic)) = −1.47 V [79]), this abstraction need not be so suprising.

Non-redox photoelimination of azide anions were also observed [32] upon irradiation of solid *trans*-$[\mathrm{Ni(PEt_3)_2(N_3)_2}]$ into LF bands at room or low (77 or 20 K) temperatures. The product of the reaction was an ion pair:

$$trans\text{-}[\mathrm{Ni(PEt_3)_2(N_3)_2}] \xrightarrow{h\nu(\mathrm{LF})} [\mathrm{Ni(PEt_3)_2(N_3)}]^+(\mathrm{N_3^-}) \quad (21)$$

In the dark, films containing the ion pairs are stable over several hours. Even more interesting is the fact that irradiation of the ion pair with UV radiation led to the back reaction regenerating the parent complex *trans*-$[\mathrm{Ni(PEt_3)_2(N_3)_2}]$. Upon irradiation of the *trans*-$[\mathrm{Ni(PEt_3)_2(N_3)_2}]$ into CT bands, dinuclear $[(\mathrm{PEt_3})(\mathrm{N_3})\mathrm{Ni}(\mu\text{-}\mathrm{N_3})\mathrm{Ni(N_3)_2(PEt_3)}]$ containing both terminal and bridging azido ligands is formed [32]. In this process azido ligands remain coordinated to the nickel(II) central atoms and the ligands $\mathrm{PEt_3}$ are eliminated. Prolonged irradiation of a film of the solid dinuclear complex leads to the loss of all ligands and generation of nickel metal film also at temperatures as low as 20 K. Contrary to the process occurring in the solid state, irradiation of *trans*-$[\mathrm{Ni(PEt_3)_2(N_3)_2}]$ dispersed in (1,2-epoxyethyl)benzene glass at 77 K gave rise to no observable photochemical reaction.

When absorbing a photon, some complexes undergo rearrangement of their structure. As an example, the complex *cis*-$[\mathrm{Pt(N_3)_2(PPh_3)_3}]$ is, along with redox processes discussed above, converted to its *trans*-isomer [63,64]. A number of photoisomerizations of platinum(II) complexes occurring from a LF excited state by a twisting mechanism, i.e. without bond-breaking and bond-forming are gathered in monographs [6,80].

3.2.5. Photochemical processes not involving azido ligand

In very rare instances of systems containing a highly redox reactive species, when using the incident radiation of a purposefully selected wavelength, the azido ligand does not participate in a photoredox processes. This is, e.g. a case of the ion pairs composed from several cobalt(III) cationic complexes and easy oxidizable $[\mathrm{B(C_6H_5)_4}]^-$ anions, irradiated into IPCT bands. The photoredox primary process occurring in irradiated systems can be, for the ion pair containing $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$, expressed as:

$$\frac{[\mathrm{Co^{III}(NH_3)_5(N_3)}]^{2+}}{[\mathrm{B(C_6H_5)_4}]^-} \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(NH_3)_5(N_3)}]^+ + [\mathrm{B(C_6H_5)_4}]^\bullet \quad (22)$$

Following the primary electron transfer between the ion pair components, the labile cobalt(II) complex formed decomposes releasing, along with ammonia molecules, also the anion $\mathrm{N_3}^-$ [5,81].

Study of $[\mathrm{M(NH_3)_5(N_3)}]^{2+}$, where M = Cr or Co documented [6] that the first photochemical deactivation step is the formation of *trans*-$[\mathrm{M(NH_3)_4(H_2O)(N_3)}]^{2+}$ caused by the photolabilization of the ammonia molecule trans to $\mathrm{N_3}^-$ due to a strong trans-effect of azido ligand. Depending on the experimental conditions, the aqua complexes generated undergo subsequent redox (M = Co) or substitution (M = Cr) reactions.

In the category of photoreactions not involving azido ligand(s) the photoejection of axial pyridine from six-coordinated $[\mathrm{Co^{III}(TPP)(Py)(N_3)}]$ occurring from its LF excited state(s) can also be introduced [82]. The photoejection is independent both of the nature of the axial acido ligand (along with azido complexes complexes with halogeno ligands were also investigated) and temperature. Other photoprocesses, such as oxidation of axial $\mathrm{N_3}^-$ from a LMCT state or more complex elimination and redox processes, may simultaneously occur.

3.2.6. Photoreactions of organic azido ligands

Contrary to a scientifically very rich area of photochemistry of organic azides, the investigation of the photoreactivity of the azido group forming part of an organic ligand is still in its infancy. An attempt to convert the azido group of azidokojic acid to cyanato group by irradiation of iron(III) azidokojato complexes in an atmosphere of CO, stimulated by Hennig's results [30] did not lead to expected products [83] and instead of iron(III) cyanatokojato complexes, undefined iron carbonyls were produced.

An example of the rare studies devoted to investigation of complexes with organic azido ligand is azidoferrocene ($\mathrm{FcN_3}$) [84,85]. Irradiation of the complex in benzene gave rise to the triplet ferrocenyl nitrene in the primary photochemical step:

$$\mathrm{FcN_3} \xrightarrow{h\nu} {}^3\mathrm{FcN} + \mathrm{N_2} \quad (23)$$

The triplet can dimerize forming azoferrocene:

$$2\,{}^3\mathrm{FcN} \rightarrow \mathrm{FeN{=}NFc} \quad (24)$$

or can react with solvent molecules via two hydrogen atom abstraction forming aminoferrocene $\mathrm{FcNH_2}$,

$${}^3\mathrm{FcN} \xrightarrow{\mathrm{R-H}} \mathrm{FcNH_2} \quad (25)$$

or can add an oxygen molecule producing nitroferrocene $\mathrm{FcNO_2}$ in high yield:

$${}^3\mathrm{FcN} + \mathrm{O_2} \rightarrow \mathrm{FcNO_2} \quad (26)$$

The last process may be exploited as a method to make nitroferrocenes No particular effect of the iron(II) central atom was observed, i.e. the azido group of azidoferrocene behaved similarly as in common organic compounds with a $\mathrm{C{-}N_3}$ bond.

Investigation of the photoredox reactivity of several iron(III) complexes containing anion(s) of kojic acid derivatives (kojic acid = 5-hydroxo-2-hydroxymethyl-4-pyran-4-one, Fig. 2a) as a chelating ligand illustrated [86–90] that the behaviour of the complexes with azidokojato ligands differs from that of other complexes. Azidokojato iron(III) complexes gave non-reproducible time dependence of iron(II) formation when

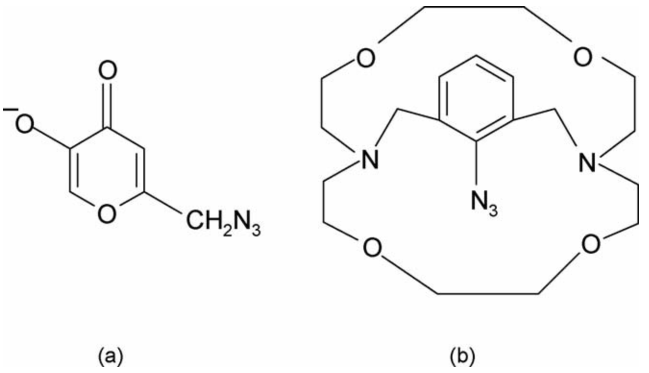

Fig. 2. Schematic structure of the azidokojic acid anion (a) and azido-functionalized cryptand (b).

exposed to UV radiation. This indicated the possibility that along with a commonly observed iron(III) photoreduction associated by oxidation of a ligand from an LMCT state, a concurrent process not involving the central atom took place. The concurrent process might be photodecomposition of the azido group.

Recently, the photochemical behaviour of an azido-functionalized cryptand (Fig. 2b) and its potassium or sodium complexes was published [91]. At low-temperature both the free ligand and its potassium(I) or sodium(I) complexes underwent photodecomposition of the azide group yielding the triplet nitrene. An inclusion of an alkali metal ion changed the zero-field splitting EPR parameters of the nitrene. The presence of coordinated alkali metal ions also influenced the course of secondary reactions, e.g. irradiation of complexes in the presence of Et_2NH led, along with aminobenzaldehyde derivative formation, to $N_3 \rightarrow NH_2$ conversion preserving the bicyclic structure of the ligand. The ligand itself (in the absence of K^+ or Na^+ ions) transformed to monocyclic aminobenzaldehyde and methyleneazepine derivatives.

4. Conclusion

Evaluation of the results obtained in the field of the photochemistry of inorganic azides and azido complexes can be concluded by some generalizations:

1. From the viewpoint of time evolution of the scientific goals and techniques applied, azido complexes have been part of the "mainstream" of photochemical research of coordination compounds, often being in the role of a member of wider groups of compounds investigated. The pioneering work of Beckman on the photodecomposition of hydrazoic acid HN_3 [13–15] may be taken as a lucid exception putting azide anion and HN_3 ahead of other similar compounds at that time.
2. Pico and femtosecond flash photolytic spectroscopic methods are needed to solve some outstanding issues in azido complex photochemistry. This may be a stimulus for further investigations. As an example, the issue of unambiguous, direct detection of inorganic nitrenes may be given.
3. A continuous transition of the research motivation from "pure" scientific investigation (represented by photosubstitutions and photoredox processes of classical pentaamino or pentacyano azido complexes [5,6]) to "industrially oriented" or at least "applied" research (photoinduced transformation of organic substances catalyzed by azido complexes) can be identified when reading published original and review papers. This transition is not reserved exclusively for azido complexes but has rather a general character.
4. Along with the traditional theoretical and practical exploitation of the knowledge gathered within the photochemical study of azido complexes, completely new applications appear from time to time. In addition to the application of astronomical importance [25] mentioned above, we may add the utilization of light + azide in the field of cell biology [92]. In the framework of research on the mechanisms of cell–cell and cell–matrix interactions it was found that the number of cells attached to glass substratum increases if HeLa cell suspension is irradiated with visible-to-near infrared radiation before plating and that treating a cell suspension with NaN_3 before irradiation significantly modifies the spectrum of cell attachment enhancement. The knowledge obtained is of key importance in understanding how to regulate proceses such as cell growth, differentiation, morphogenesis, wound repair, formation of metastases, etc. One should not be surprised by appearance of another field of application in the future.

Acknowledgements

This work was financially supported by the grants VEGA 1/2452/05 and APVT-20-005504.

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