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Photoreactivity of gold complexes

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Abstract

The light sensitivity of gold compounds has been known since 1737. More recent observations have led to a deeper understanding of the photochemistry of gold complexes,

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which are discussed on the basis of selected examples. Light sensitive Au(I) and Au(III) compounds are classified according to the nature of reactive excited states: metal-centered (MC), ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), metal-to-metal charge transfer (MMCT) and intraligand (IL). Accordingly, some basic information on the electronic spectra of gold complexes including luminescence spectra is provided. The photochemistry is described in more detail. Essentially, our own observations are reported but some relevant observations of other groups are also included.

Keywords: Photochemistry; Gold complexes; Electronic spectra

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1. Introduction

The light sensitivity of gold compounds has been known since 1737 [1]. Despite such early observations [2,3] progress has been rather slow in this field [4]. During the last decade we have studied the photoreactivity of several gold complexes. The present report is a short account of this work. While this subject is rather interesting in its own right, the potential applications of the photochemistry of gold compounds are significant in other areas. For example, the photochemical deposition of metallic gold can be utilized for the fabrication of electronic devices [5,6]. Moreover, gold complexes play an important role in medicine as antiarthritic, antiviral, cytotoxic and antiinfective drugs [7,8]. The light stability is now considered to be a critical property of drugs [9]. In addition, gold compounds may be catalytically active. Recently, cations of the type $[LAu^{I}(solvent)]^{+}$ with $L = PR_3$, AsR_3 and $P(OR)_3$ have been observed to catalyze the addition of alcohols to alkynes [10]. Since $LAu^{I}CH_3$ as the precursor of the active catalyst is certainly light sensitive (see below) its photochemical behavior must be taken into account. In this context it is quite surprising that so little is known on the photoreactivity of gold complexes in contrast to their photoluminescence which has been studied in great detail [11,12]. Both properties serve to characterize excited states.

While gold exists in oxidation states from $-$I to $+$V only Au(I) and Au(III) complexes which constitute the majority of gold compounds are treated in this review. Frequently, the lowest-energy excited state determines the photoluminescence and photochemistry of a particular compound. In the following discussion gold compounds are thus classified according to the nature of their lowest excited states which may be of the metal-centered (MC), ligand-to-metal charge transfer (LMCT), metal-to-ligand charge transfer (MLCT), metal-to-metal charge transfer (MMCT), ligand-to-ligand charge transfer (LLCT), intraligand (IL) and intraligand charge transfer (ILCT) type. While the photoreactivity which originates from these excited states is emphasized in this article some basic information on the electronic spectra of gold complexes is also provided. However, the emission behavior is illustrated only by a few selected examples since it has been reviewed recently [11,12]. Essentially, our own observations are presented in this report but some relevant results of other groups are included, too.

2. Gold(I)

2.1. Absorption spectra

Generally, gold(I) complexes have linear structures. In the free Au(I) ion with its d^{10} electron configuration the frontier orbitals are the filled 5d orbitals followed by the empty 6s and 6p orbitals. Accordingly, ligand field (LF) excited states are not available but low-energy MC 5d → 6s and 5d → 6p transitions are accessible. The longest-wavelength absorption of simple Au(I) complexes such as $[AuCl_2]^-$ (λ_{max} = 246 nm), $[AuBr_2]^-$ (256 nm) [13] and Au(CO)Cl (250 nm) (Fig. 1) [14] are apparently of the ds type.

Since Au(I) is oxidizing as well as reducing, LMCT and MLCT transitions could occur at reasonable energies. It follows that Au(I) complexes with more reducing ligands should display LMCT absorptions at long wavelength. These LMCT transitions may mix with MC transitions of the same symmetry. Corresponding absorptions have been identified in azide, iodide and thiolate complexes: $[Au(N_3)_2]^-$ (λ_{max} = 218 nm) [15], $[AuI_2]^-$ (361 nm) [13] and $[Au(SH)_2]^-$ (250 nm) (Fig. 2) [16].

In the spectra of Au(I) complexes with π-acceptor ligands low-energy MLCT absorptions should be observed. Indeed, Au(I) complexes with simple π-acceptor ligands such as cyanide, phosphines and isocyanides display MLCT absorptions in their electronic spectra. However, these MLCT bands appear at very short wavelength. Examples are $[Au(CN)_2]^-$ (λ_{max} = 240 nm) [17], $[Au(PEt_3)_2]^+$ (251 nm) [18], $Au(PEt_3)Cl$ (235 nm) [18] and $[Au(CNEt)_2]^+$ (243 nm) [19]. Moreover, the MLCT acceptor MOs are composed of π* (ligand) and p (gold) orbitals in these cases. Accordingly, the MLCT transitions are heavily mixed with MC dp transitions. The extent of CT is then not quite clear. Consequently, the examination of polypyridyl complexes [20,21] which provide π* acceptor orbitals of the ligands at much lower energies should yield more reliable information on the existence of MLCT transitions in Au(I) complexes. Unfortunately, not much is known on Au(I)–polypyridyl complexes. Anions of the type $[Au^I(CN)_2(polypyridyl)]^-$ with polypyridyl = 2,2′-

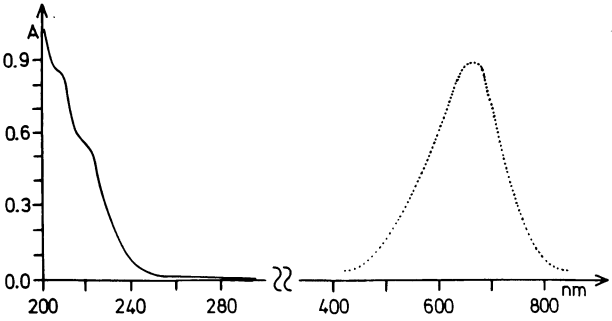


Fig. 1. Electronic absorption (—) and emission (· · · ·) spectra of Au(CO)Cl at room temperature. Absorption: 1.74×10^{-4} M in dry acetonitrile under argon, 1 cm cell. Emission: in the solid state, λ_{exc} = 280 nm, intensity in arbitrary units.

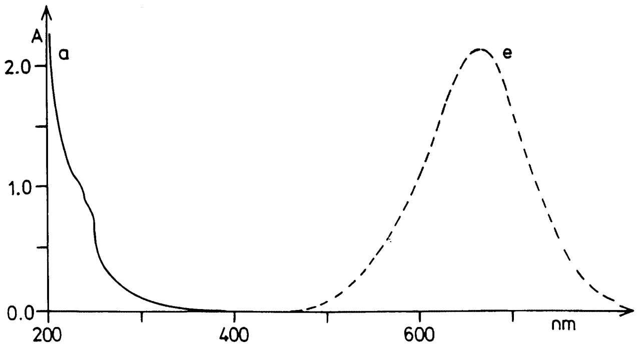


Fig. 2. Electronic absorption (a, —) and emission (e, · · · ·) spectra of $(Bu_4N)[Au(SH)_2]$. Absorption: 3.75×10^{-4} M in dry acetonitrile under argon at r.t., 1 cm cell. Emission: in toluene at 77 K, $\lambda_{exc}=300$ nm, intensity in arbitrary units.

bipyridyl and 9,10-phenanthroline were reported [22], but their identity is questionable [23,24]. MLCT absorptions were not detected in these cases. In this context it must be kept in mind that the reducing properties of Au(I) are based on the $Au^{+/3+}$ redox couple while an optical MLCT transition leads to the generation of Au(II). This CT may require rather high energies. The assumption that Au(I) is indeed a very weak CT donor was recently verified by the examination of an outer sphere charge transfer (OSCT) absorption in the ion pair. $PQ^{2+}[Au(CN)_2]^-$ (PQ^{2+} = paraquat^{2+} or N,N'-dimethyl-4,4′-bipyridinium^{2+}) [24]. Although paraquat^{2+} is a strong acceptor the (Au(I)→paraquat^{2+}) OSCT band ($\lambda_{max}=331$ nm) appears at rather short wavelength (Fig. 3).

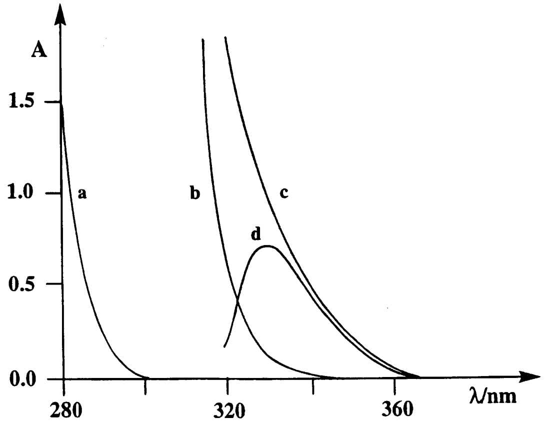


Fig. 3. Electronic absorption spectra of: (a) aqueous 4.3×10^{-2} M $K[Au(CN)_2]$; (b) 4.3×10^{-2} M $(PQ)Cl_2$ as separate solutions in 1 cm cells; (c) as a mixture in a 2 cm cell; and (d) the difference spectrum (d = c − a − b) at room temperature.

In polynuclear Au(I) complexes a weak but direct metal–metal interaction may occur. This is illustrated by the complex $[Au_2(dppm)_2]^{2+}$ which contains bis-(diphenylphosphino) methane (dppm) as bridging ligand [25–27]. The gold–gold interaction leads to a σ overlap of 5d and 6p orbitals. The HOMO and LUMO are σ_d^* and σ_p^b orbitals, respectively. In the ground state with the electron configuration $(\sigma_d^b)^2(\sigma_d^*)^2$ a metal–metal bond does not exist. In contrast, in the dp excited state with the configuration $(\sigma_d^b)^2(\sigma_d^*)^1(\sigma_p^b)^1$gold–gold bond is formed. The corresponding MC dp absorption of $[Au_2(dppm)_2]^{2+}$ appears at $\lambda_{max} = 292$ nm. A variety of other polynuclear Au(I) complexes are characterized by low-energy transitions of the same type [11,12]. The oligomerization of $[Au(CN)_2]^-$ in solution leads also to the occurrence of new long-wavelength absorptions [28].

In heteronuclear complexes Au(I) can form a direct but polar σ bond to another metal. In the case of $(Ph_3P)Au^I$–$Co^{-I}(CO)_4$ metal–metal interaction takes place by the overlap of the 6s (Au) orbital and the $3d_z^2$ (Co) orbital which is located at much lower energies [29]. Accordingly, the HOMO is dominated by the $3d_z^2$ (Co) orbital while the LUMO contains a much larger portion of the 6s (Au) orbital. The σσ* transition can thus be also viewed as Co(−I)→Au(I) MMCT transition. Ph_3PAu^I–$Co^{-I}(CO)_4$ shows this MMCT absorption at 305 nm (Fig. 4) (also see Eqs. (11) and (12).

In some cases the lowest-energy transitions are of the IL type. Such IL bands appear in the absorption spectra of $[Au^I(C{\equiv}C\text{–}Ph)_2]^-$ ($\lambda_{max} = 269$ nm) [30] and $[(Au^IPPh_3)_2$-μ-bbzim] (340 nm) with 2,2′-bibenzimidazolate ($bbzim^{2-}$) as bridging ligand [31].

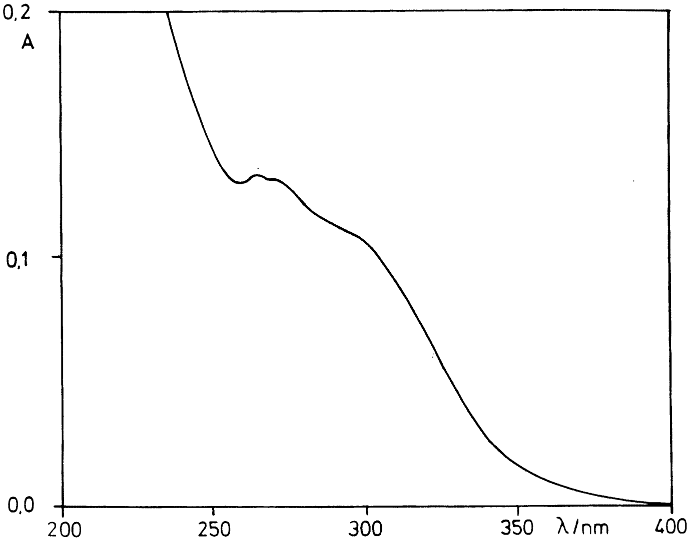


Fig. 4. Electronic absorption spectrum of 2.4×10^{-5} M $[Ph_3Au$–$Co(CO)_4]$ in hexane under argon at r.t., 1 cm cell.

2.2. Emission spectra

As mentioned above the emission behavior of Au(I) complexes has been studied by many groups. Although the nature of the luminescence is not yet completely understood a variety of different excited states has been suggested to be emissive [32]. Typical examples are described in this section. As a general rule it is assumed that the lowest-energy excited state which is populated in absorption is also the emissive state. Of course, this notion does not include the spin multiplicity. Owing to the heavy atom effect of gold the longest-wavelength emission is generally a phosphorescence.

It follows from these considerations that the photoluminescence of $[AuCl_2]^-$ ($\lambda_{max} = 687$ nm) and $[AuBr_2]^-$ (660 nm) in ethanol glasses at 77 K originates from a MC ds triplet [33]. However, the huge energy difference between the longest-wavelength absorption (see above) and the emission requires an explanation. It is possible that the emissive species are oligomeric $[AuX_2^-]_n$ which exist in small concentrations even in dilute solution. This supposition is based on recent observations on $[Au(CN)_2]^-$ [28]. While the monomer is apparently not emissive luminescent oligomers are formed at formal concentrations of $[Au(CN)_2]^-$as low as 10^{-5} M. Solid Au(CO)Cl shows a MC phosphorescence ($\lambda_{max} = 663$ nm) also under ambient conditions (Fig. 1) [14]. The room temperature (r.t.) emission of solid Au(TPA)Cl with TPA = 1,3,5-triaza-7-phosphaadamantane at $\lambda_{max} = 643$ nm is assumed to come from a ds triplet, too [34].

In other cases MC dp states are lower in energy than ds states. Such a stabilization of 6p orbitals of gold can be achieved by π-acceptor ligands. Several three-coordinate gold–phosphine complexes belong to this category and emit from dp triplets, e.g. $[Au(PPh_3)_3]^+$ ($\lambda_{max} = 512$ nm) [35] and $[Au_2(dcpe)_3]^{2+}$ with dcpe = bis(dicyclohexylphosphino)ethane ($\lambda_{max} = 508$ nm) [36] in CH_3CN at r.t. The latter complex is binuclear but contains isolated $Au^I(phosphine)_3$ moieties.

A stabilization of 6p Au orbitals occurs also by direct gold–gold interaction in polynuclear complexes which contain bridging phosphines. Compounds such as $[Au_2(dppm)_2]X_2$ with dppm = bis(dimethylphosphino)methane ($\lambda_{max} = 593$ nm, X = BF_4 [26] and 565 nm, X = ClO_4) [25–27] and $[Au_3(dmmp)_2](ClO_4)_3$ with dmmp = bis(dimethylphosphinomethyl)-methylphosphine ($\lambda_{max} = 580$ nm) [37] in CH_3CN at r.t. have been suggested to phosphoresce from such dp triplets.

With strong reducing ligands the lowest and thus the emitting excited state may be of the LMCT type. In some cases it has been suggested that the phosphorescence originates from LMCT states which are mixed with MC states. A variety of Au^I–thiolate complexes seem to emit from such LMCT or LMCT/MC triplets, e.g.

$Au^I(TPA)(SPh)$, $\lambda_{max} = 596$ nm (77 K) [38], TPA = 1,3,5-triaza-7-phosphaadamantane; $Au^I(PEt_3)SR$ (auranofin), $\lambda_{max} = 594$ nm (77 K) [32], RS^- = 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosato-5$[Au^I(SH)_2]^-$; $\lambda_{max} = 646$ nm (Fig. 2) [16].

Polynuclear gold(I)–thiolate complexes emit also from (thiolate → Au^I) LMCT triplets, e.g.

$Au^{I}_{2}(dppe)(p\text{-tc})_2$, $\lambda_{max} = 495$ nm [39], dppe (diphos) = bis(diphenylphosphino)ethane; p-tc$^-$ = p-thiocresolate.

Sometimes IL states occur at lowest energies provided the ligand itself has available low-energy excited states. Various Au(I) complexes seem to luminesce from IL triplets, e.g.

$[Au^{I}(C{\equiv}C–Ph)_2]^-$, $\lambda_{max} = 450$ nm [30]; $Au^{I}_{2}(dcpn)(C{\equiv}C–C_6H_4\text{-}p\text{-}Ph)_2$, $\lambda_{max} = 753$ nm [40], dcpn = 1,8-bis(dicyclohexylphosphino)naphthalene.

while the phosphorescence of $[Au^{I}(C{\equiv}C–Ph)_2]^-$ originates from the acetylide ππ* state [30] the dcpn complex emits from the dcpn triplet [40]. In this case the emitting state is apparently of the ILCT type. It is populated by the promotion of an electron from the Au–P σ-bond to the π* orbitals of the naphthalene moiety.

Occasionally, the interaction of heavy metals with ligands is not strong enough to completely quench the IL fluorescence by enhanced intersystem crossing, e.g.

$Au^{I}_{2}(PPh_3)_2(\mu\text{-bbzim})$, $\lambda_{max} = 360$ nm (fluorescrence), $\lambda_{max} = 473$ nm (phosphorescence) [31], bbzim^{2-} = 2,2′-bibenzimidazolate.

Various heteronuclear Au(I) complexes such as $[Ir^{I}_{2}Au^{I}Cl_2(CO)_2(\mu\text{-dpma})]^+$ with dpma = bis(diphenylphosphino)methylarsine ($\lambda_{max} = 606$ nm) also have been observed to emit under ambient conditions [41]. It has been suggested that the emission comes from a MC excited state which is based on the metal–metal interaction in the heteronuclear M_3 moiety.

2.3. Photochemistry

2.3.1. Metal-centered excited states

LF (or dd) excited states of complexes with d^n metals ($n = 1–9$) are well known to initiate photosubstitutions of ligands. This photoreactivity is largely based on the population of M–L σ-antibonding d-orbitals by electronic excitation. In the case of d^{10} metals the presence of low-energy MC ds excited states should have similar consequences since the metal s-orbital is also of the M–L σ* type. In analogy to a variety of metal–carbonyl complexes which release CO upon LF excitation [42] the complex Au(CO)Cl is then expected to show the same photochemical behavior. Indeed, ds excitation ($\lambda_{irr} = 280$ nm) of Au(CO)Cl leads to a photolysis [14]. The primary photochemical step proceeds apparently according to the equation:

$$Au(CO)Cl \xrightarrow{h\nu} AuCl + CO \tag{1}$$

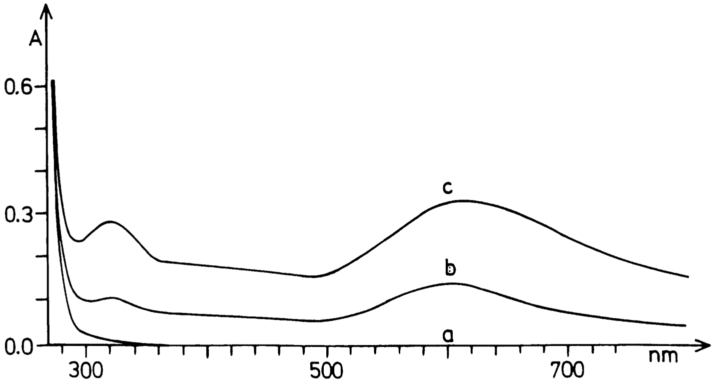


Fig. 5. Spectral changes during the photolysis of 1.08×10^{-3} M Au(CO)Cl in dichloromethane under argon at r.t. after 0 (a), 2 and 5 min (c) irradiation time with $\lambda_{irr} > 280$ nm (HBO 100 W/2. cut-off Schott WG 305), 1 cm cell.

In non-coordinating solvents such as CH_2Cl_2, AuCl is not stable but disproportionates:

$$3AuCl \rightarrow AuCl_3 + 2Au^0 \tag{2}$$

The concomitant spectral changes (Fig. 5) indicates the formation of colloidal gold ($\lambda_{max} \sim 600$ nm). Gold(III) chloride is formed with $\phi = 0.02$ at $\lambda_{irr} = 280$ nm. In acetonitrile this reaction is less efficient since the solvent stabilizes AuCl by coordination.

While excited state electron transfer can lead to the formation of persistent photoproducts it is frequently completely reversible. Accordingly, such complexes do not appear to be light sensitive. In these cases excited-state electron transfer is often monitored by luminescence quenching of the complex in the presence of suitable electron donors or acceptors. Occasionally, the formation of electron-transfer products as short-lived intermediates is detected by flash photolysis.

The binuclear cation $[Au_2(dppm)_2]^{2+}$ with dppm = bis(diphenylphosphino)-methane emits from a MC (Au–Au) excited state. This emission is quenched by electron donors (e.g. tetramethyl-*p*-phenylenediamine) as well as acceptors such as methylviologen (or paraquat) and organic halides [25,27]. Since the Au_2^I moiety is involved in the excited state electron transfer mixed-valence Au^IAu^0 and Au^IAu^{II} compounds, respectively, should be formed as primary photoproducts. Persistent products are not formed because the initial electron transfer is completely reversed by thermal recombination. The heterobimetallic complex $[Au^IPt^{II}(dppm)_2(CN)_2]^+$ also undergoes excited state electron transfer to pyridinium acceptors [43]. However, the excitation and photoredox processes seem mainly to be associated with the platinum center in this case.

In the presence of oxygen the trinuclear complex $[Au_3(dmmp)_2]^{3+}$ with dmmp = bis(dimethylphosphinomethylphosphine) induces the photochemical cleavage of DNA [44]. It is assumed that a MC dp triplet transfers an electron or energy to oxygen. Superoxide or singlet oxygen might then attack and cleave DNA.

The complexes $[AuX_2]^-$ with X = Cl and Br are also photoactive upon ds excitation [30]. However, a photosubstitution of X^- does not take place but the complex anions undergo a photooxidation which is initiated by excited-state electron transfer. The ds excited complexes are apparently able to donate electrons to suitable acceptors such as CH_2Cl_2 or oxygen. The reduction of CH_2Cl_2 leads to the irreversible release of chloride which is then attached to Au(III) as final oxidation product. In neat CH_2Cl_2 the photooxidation of $[AuCl_2]^-$ to $[AuCl_4]^-$ was quite efficient with $\phi \sim 10^{-1}$ ($\lambda_{irr} = 254$ nm) while at lower concentrations of CH_2Cl_2 the quantum yields are much smaller, e.g. $\phi \sim 10^{-4}$ in CH_3CN with 0.02 M CH_2Cl_2. Molecular oxygen serves also as a photooxidant. In air-saturated acetonitrile in the presence of a chloride excess $[AuCl_4]^-$is formed, too:

$$[AuCl_2]^- + 2Cl^- \xrightarrow{h\nu/O_2} [AuCl_4]^- + 2e^- \quad (3)$$

But this photooxidation is not very efficient ($\phi \sim 10^{-5}$). The anion $[AuBr_2]^-$ undergoes the same type of photooxidation upon ds excitation. In aerated acetonitrile which contains additional bromide $[AuBr_4]^-$ is formed with $\phi \sim 10^{-3}$ at $\lambda_{irr} = 280$ nm.

2.3.2. Metal-to-ligand charge transfer excited states

Very little is known on the reactivity of MLCT states of Au(I) complexes. However, it has been shown that MLCT excitation of $[Au(CN)_2]^-$ leads to photolysis under suitable conditions [45]. In the presence of chloride and molecular oxygen $[Au(CN)_2]^-$ undergoes a photooxidation in analogy to that of $[AuX_2]^-$ (X = Cl and Br):

$$[Au^I(CN)_2]^- + 2Cl^- \xrightarrow{h\nu/O_2} [Au^{III}(CN)_2Cl_2]^- \quad (4)$$

The MLCT excited state of $[Au(CN)_2]^-$ is also apparently able to transfer an electron to O_2. Gold(II) may be formed as an intermediate. Product formation takes then place by disproportionation to Au(I) and Au(III) or by further oxidation to Au(III) in a second electron-transfer step. In air-saturated solution $[Au^{III}(CN)_2Cl_2]^-$ is formed with $\phi \sim 10^{-4}$ at $\lambda_{irr} = 254$ nm.

2.3.3. Ligand-to-metal charge transfer excited states

With more reducing ligands the lowest excited states of Au(I) complexes are of the LMCT type. This notion applies, for example, to $[Au(N_3)_2]^-$. In agreement with the general behavior of LMCT states Au(I) undergoes a photoreduction [15]

$$[Au^I(N_3)_2 \xrightarrow{h\nu} Au^0 + 1.5N_2 + N_3^- \quad (5)$$

This photoredox decomposition is very efficient. In acetonitrile $[Au(N_3)_2]^-$ disappears with $\phi = 0.2$ at $\lambda_{irr} = 254$ nm. Metallic gold is generated as a colloid. It is identified and characterized by its plasmon absorption which causes the striking red to violet colors of gold colloids. Since photoreactions can be controlled nicely by the appropriate choice of parameters such as light intensity, temperature and substrate concentration the photolytic generation of colloidal gold should be superior over thermal procedures which are generally utilized for applications.

LMCT excited states of gold(I) complexes with thiolates or sulfides as ligands are also reactive. The photolysis of $\mathrm{Au(SMe_2)Cl}$ leads again to the photoreduction of gold(I) [16]. The primary photochemical step is assumed to proceed according to the equation:

$$\mathrm{Au(SMe_2)Cl} \xrightarrow{h\nu} \mathrm{Au^0} + {}^{\bullet}\mathrm{SMe_2^+} + \mathrm{Cl^-} \tag{6}$$

while colloidal gold is finally formed the oxidation products are unknown. It is a reasonable suggestion that the oxidized ligand radical cation transfers a methyl cation to chloride and dimerizes to the disulfide:

$${}^{\bullet}\mathrm{SMe_2^+} + \mathrm{Cl^-} \rightarrow \tfrac{1}{2}\mathrm{Me_2S_2} + \mathrm{MeCl} \tag{7}$$

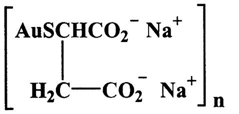
In ethanol the photoreduction takes place with $\phi = 0.03$ at $\lambda_{\mathrm{irr}} = 366$ nm.

LMCT excitation of $[\mathrm{Au(SH)_2}]^-$ does not yield persistent redox products but takes place according to the equation [16]:

$$2[\mathrm{Au(SH)_2}]^- \xrightarrow{h\nu} \mathrm{Au_2S} + \mathrm{H_2S} + \mathrm{HS^-} \tag{8}$$

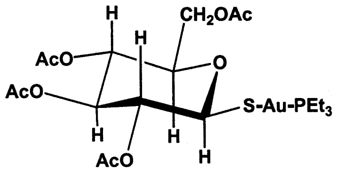
A ${}^{\bullet}\mathrm{SH}$ radical and $\mathrm{Au^0}$ should be also formed in the primary photochemical step. However, the great stability of $\mathrm{Au_2S}$ apparently favors a recombination. In ethanol this photolysis proceeds with $\phi = 0.01$ at$\lambda_{\mathrm{irr}} = 254$ nm.

The antiarthritic drugs myochrysin and auranofin are Au(I)–thiolate complexes, too:



$$\left[\begin{array}{l} \mathrm{AuSCHCO_2^-\ Na^+} \\ \quad\ \ | \\ \mathrm{H_2C{-}CO_2^-\ Na^+} \end{array}\right]_n$$

myochrysin



auranofin

Both compounds are light sensitive [32]. The photoreactivity has been attributed to LMCT excited states. The photolysis of myochrysin leads to the formation of $\mathrm{Au_2S}$ in analogy to that of $[\mathrm{Au(SH)_2}]^-$. In the case of auranofin simple photoproducts such as colloidal gold or $\mathrm{Au_2S}$ were not detected. While $\mathrm{Au^0}$ and an oxidized thiolate radical should be formed in the primary photochemical step, product formation may take place by various secondary processes which are facilitated by the complicated composition of auranofin.

The photochemical properties of phosphine complexes of the type $\mathrm{CH_3Au^IPR_3}$ [46–48] can be also attributed to reactive LMCT states. Although their electronic spectra have not yet been reported and discussed these compounds should have available low-energy $\mathrm{CH_3^-} \rightarrow \mathrm{Au^1}$ LMCT states since carbanions are quite reducing ligands. It is well known that organometallics which contain M–L σ bonds are characterized by long-wavelength LMCT absorptions [49]. Generally, LMCT excitation of such complexes leads to the reduction of the metal and oxidation of the carbanion in the primary photochemical step [50]. This homolytic M–L bond cleavage occurs also upon UV irradiation of $\mathrm{CH_3AuPR_3}$:

$$\mathrm{CH_3 - Au^IPR_3} \xrightarrow{h\nu} \mathrm{CH_3^{\bullet}} + \mathrm{Au^0PR_3} \tag{9}$$

The fate of this radical pair depends on the reaction conditions. When the photolysis is carried out in the presence of nitrosobenzene the methyl radicals can be intercepted by this spin trap and identified by ESR spectroscopy [48]. In benzene solutions, which contain tetrafluoroethylene an insertion takes place [46]:

$$\mathrm{CH_3Au^IPR_3 + C_2F_4 \xrightarrow{h\nu} CH_3 - CF_2 - CF_2Au^IPR_3} \tag{10}$$

In $CHCl_3$ solutions the photolysis of CH_3AuPR_3 leads to the formation of $Au(PR_3)Cl$ [47].

Various radical reactions involving the solvent have been identified by CIDNP-NMR spectroscopy. However, the significance of these results is not clear because in $CHCl_3$ solutions the photolysis of the solvent must be taken into account unless light absorption by $CHCl_3$ is completely excluded [51].

2.3.4. *Metal-to-metal charge transfer excited states*

Au(I) forms polar σ-bonds to other metals including main-group metals. Accordingly, σσ* excitation can be also viewed as a MMCT transition [49]. Such σ-bonds can be split homolytically by σσ* excitation [50]. One metal is reduced while the other is oxidized in the primary photochemical step. The photolysis of $(Ph_3P)Au^I–Co^{-I}(CO)_4$ is initiated by this type of MMCT transition [29]:

$$\mathrm{(Ph_3P)Au^I - Co^{-I}(CO)_4 \xrightarrow{h\nu} PPh_3 + Au^0 + Co^0(CO)_4} \tag{11}$$

$$\mathrm{2Co^0(CO)_4 \rightarrow Co_2^0(CO)_8} \tag{12}$$

$Co^{-I} \rightarrow Au^I$ CT excitation finally leads to the formation of metallic gold and cobalt carbonyl. In THF the photolysis is quite efficient with $\phi = 0.1$ at $\lambda_{irr} = 333$ nm.

An analogous behavior is observed for $(R_3P)_3Au^I–Sn^{II}Cl_3$ with $R = Ph$ and OCH_3. $Sn^{II} \rightarrow Au^I$ CT excitation is again associated with a homolytic splitting of the Au–Sn σ-bond [52]:

$$\mathrm{(R_3P)_3Au^I - Sn^{II}Cl_3 \xrightarrow{h\nu} 3R_3P + Au^0 + Sn^{III}Cl_3} \tag{13}$$

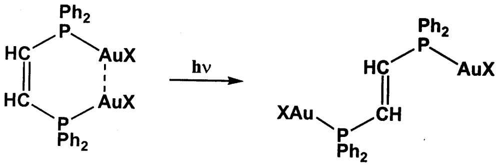
$SnCl_3$ is not stable but may disproportionate to $SnCl_2$ and $SnCl_4$. As an alternative $SnCl_3$ could thermally reduce Au(I). Both pathways yield the same final products:

$$\mathrm{2(R_3P)_3Au^I - Sn^{II}C1_3 \xrightarrow{h\nu} 6PR_3 + 2Au^0 + SnCl_2 + SnCl_4} \tag{14}$$

In CH_3CN this photolysis proceeds with $\phi = 0.41$ at $\lambda_{irr} = 282$ nm.

2.3.5. *Intraligand excited states*

Olefin complexes undergo a variety of photochemical reactions including *trans*/*cis* isomerization of the olefin ligand [53]. Frequently, these isomerizations are induced by ππ* IL excitation. Binuclear gold(I) complexes of the type $Au_2X_2(dppe)$ with $X =$ halogen and dppe = bis(diphenylphosphino)ethylene undergo a *cis* to *trans* photoisomerization at the olefinic double bond [54]:



In the ground state the *cis* isomer is apparently stabilized by an aurophilic interaction between both Au^+ ions. The photoactivity seems to originate from a $\pi\pi^*$ IL (ethylene) excited state which is strongly modified by the complex fragments [55]. Interestingly, there is no ethylene IL contribution to the lowest-energy excited states of the *trans* isomer. This explains the absence of any *trans* → *cis* photoisomerization of the complex.

The lowest-energy excited state of alkynyl (or acetylide) gold(I) complexes are frequently of the $\pi\pi^*$ (C≡C) IL type (see above). The complexes $Au(PPh_3)(C{\equiv}CPh)$ [27] and $Au_3(dmmp)(C{\equiv}CPh)_3$ [40] with dmmp = bis(dimethylphosphinomethyl)methylphosphine are characterized by such emissive IL states. This phosphorescence is quenched by electron acceptors including pyridinium cations (e.g. methyl viologen or paraquat). The occurrence of an excited-state electron transfer has been confirmed by flash photolysis which leads to the generation of a reduced methyl viologen radical. A facile back electron transfer seems to prevent the formation of persistent photoproducts.

Another Au(I) acetylide complex undergoes an irreversible photolysis which should be also induced by IL excitation. Gold(I) phenylacetylide is soluble in coordinating solvents where it may exist as two-coordinate complex solvent–Au–C≡CPh. These solutions are rather light sensitive [56]. Upon irradiation the yellow color changes to black. Although the photoproducts were not identified it may be speculated that the black color is caused by polyacetylene doped with impurities.

Finally, the light sensitivity of the binuclear complex B_{12}-μ-NC–Au^ICN should be mentioned [57]. This compound contains vitamin B_{12} with Co(III) as metal center and cyanide as bridging ligand. Irradiation of an aqueous solution simply leads to a substitution:

$$B_{12}\text{-}\mu\text{-NC}-AuCN + H_2O \xrightarrow{h\nu} [B_{12}-H_2O]^+ + [Au(CN)_2]^- \qquad (15)$$

The lowest excited states of the intensely colored binuclear complex are apparently associated with the B_{12} moiety. The photoreactivity is quite similar to that of other B_{12} derivatives [58].

3. Au(III)

3.1. Absorption spectra

Au(III) with its d^8 electronic configuration forms a variety of square-planar complexes. Accordingly, LF transitions occur [20]. Since Au^{III} is oxidizing low-energy LMCT transitions are quite important. However, MLCT transitions do not play any role owing to the lack of reducing properties of Au(III). For example, $[Au(CN)_4]^-$ does not show any absorption maximum above 200 nm [59,60] while cyanide complexes of reducing metals such as $[M(CN)_6]^{4-}$ with M = Fe, Ru, Os display MLCT bands at relatively long wavelength [20].

The electronic spectra of various anions of the type $[AuX_{4-n}Y_n]^-$ ($n = 0$–4 and $X^- =$ halide$^-$, Y = pseudohalide) have been studied [59–61]. Unfortunately, complete assignments were not reported. Complications are caused by the appearance of LMCT and less intense LF bands at comparable energies. Moreover, weak absorptions of forbidden transitions are frequently obscured by stronger bands. Spectra were recorded at various temperatures and in different solvents. In CH_3CN and at r.t. LF bands were identified in a few cases. The longest-wavelength LF absorption of $[AuCl_4]^-$ and $[AuBr_4]^-$ appear at 400 nm (shoulder) and 460 nm (shoulder), respectively. Owing to their higher intensity LMCT absorptions were assigned with more confidence. The longest-wavelength LMCT bands of Au(III) complexes in CH_3CN occur in their near UV or with more reducing ligands even in the visible spectral region, e.g. [61]

	λ_{max} (nm)	ε
$[AuCl_4]^-$	323	5800
$[AuBr_4]^-$	476	1230 shoulder
$[Au(N_3)_4]^-$	331	23 900 [62,63]
trans-$[Au(CN)_2Cl_2]^-$	292	1060
trans-$[Au(CN)_2Br_2]^-$	357	650 shoulder
trans-$[Au(CN)_2I_2]^-$	444	920 shoulder

The spectra of $[Au^{III}(dbbpy)(tdt)]^+$ and $[Au^{III}(\eta^2\text{-}C,N\text{-ppy})(tdt)]$ in CH_2Cl_2 with dbbpy = dibutyl-2,2′-bipyridyl, η^2-*C*,*N*-ppy$^-$ = *o*-C-deprotonated 2-phenylpyridine and tdt^{2-} = 4-toluene-1,2-dithiolate display fairly intense absorptions in the visible region at $\lambda_{max} = 440$ nm ($\varepsilon = 2300$) and 408 nm (3200), respectively [64]. These bands may be attributed to tdt^{2-} to Au(III) LMCT or tdt^{2-} to dbbpy/η^2-*C*,*N*-ppy LLCT transitions. Any MLCT character is quite unlikely as outlined above.

The absorption spectra of various 1,2-diimine complexes of the general composition $[Au^{III}(1,2\text{-diimine})X_2]^+$ in CH_3CN with 1,2-diimine = 2,2′-bipyridyl, 9,10-phenanthroline, 4,7-diphenyl-9,10-phenanthroline and X = mesityl, CH_2SiMe_3, Cl have been recently reported [65]. The spectra are characterized by intense 1,2-diimine IL bands which display a typical vibrational pattern, e.g.

	λ_{max} (nm)	ε
$[Au(bipy)Cl_2]^+$	282	12 275
	308	5085
	324	4590
$[Au(bipy)(mesityl)_2]^+$	307	15 070
	319	15 680

The occurrence of other bands such as LF absorptions which might appear at longer wavelength was not reported.

Typical long-wavelength IL bands dominate also the spectra of Au(III) porphyrin [21] and dithizonate complexes, e.g.

$[Au(TPP)^+$ in CH_2Cl_2, λ_{max}
$= 408$ nm (Soret band); 520 nm (Q band) [66], TPP^{2-}
$=$ tetraphenylporphyrin dianion; $[Au(HDZ)Cl_2]$ in $CHCl_3$, λ_{max}
$= 540$ nm; 570 nm [67], $HDZ^- =$ dithizonate monoanion.

3.2. Emission spectra

In contrast to Au(I), Au(III) complexes have been rarely observed to emit. In all cases the luminescent excited states are apparently IL triplets. Some complexes show this IL phosphorescence also at r.t. Frequently, these IL emissions are associated with 1,2-diimine (or polypyridyl) ligands, e.g.

$[Au(bipy)(mesityl)_2]^+$ in CH_3CN, r.t., λ
$= 506$ nm ($\tau = 0.6$ μs); $[Au(bipy)Cl_2]^+$ solid, r.t., 457 nm ($\tau = 0.3$ μs) [65].

The vibrational structure of these emission bands indicates the 1,2-diimine participation. At 77 K a solid sample of the complex $[Au(bipy)Cl_2]^+$ show an additional long-wavelength emission at $\lambda_{max} = 640$ nm which may belong to an excimer.

Au(III) porphyrins display also an IL phosphorescence, e.g.

$[Au(TPP)]^+$ in ethanol/glycerol, 77 K $\lambda_{max} = 700$ and 780 nm, $\tau = 63$ and 184 μs; $\phi \sim 6 \times 10^{-3}$ [66].

At r.t. in solution an emission is not observed. In all cases the appearance of an IL phosphorescence indicates the absence of lower-energy excited states of different origin such as LF or LMCT states.

3.3. Photochemistry

The light sensitivity of Au(III) complexes has a long history [2,3]. The oldest observations on the photo chemical reduction of gold(III) chloride to elemental gold had been reported by Hellot in 1737 [1] and Scheele in 1777 [68]. However, in most cases the experimental parameters (e.g. light-absorbing species, electronic spectra, irradiating wavelength, chemical intermediates) were not or only ill defined. Some general conclusions based on more recent studies will be discussed below.

3.3.1. Substitutions

While a variety of Pt(II) complexes is well known to undergo a photosubstitution upon LF excitation [69] a photochemical ligand exchange of an isoelectronic Au(III) complex has been observed only recently [45]:

$$[Au(CN)_2Cl_2]^- + 2Cl^- \xrightarrow{h\nu} [AuCl_4]^- + 2CN^- \quad (16)$$

This photosubstitution proceeds in CH_3CN at $\lambda_{irr} = 254$ nm. Since the light is absorbed by a LMCT band ($\lambda_{max} = 292$ nm) the photolysis may originate from a LMCT state. Photosubstitutions induced by LMCT excitation are well known [50].

However, it seems more likely that the LMCT state undergoes a facile deactivation to a lower-energy LF state which initiates the photosubstitution. Unfortunately, the study of the electronic spectrum of $[Au(CN)_2Cl_2]^-$ was only concerned with LMCT transitions [61].

3.3.2. Redox reactions

A variety of d^8 complexes undergoes reductive eliminations to d^{10} complexes upon LMCT excitation. This reaction type applies also to Au(III) compounds. For example, it has been shown that LMCT excitation ($\lambda_{irr} = 333$ nm) of $[Au(N_3)_4]^-$ in organic solvents leads to a clean and efficient photolysis ($\phi = 0.51$ in CH_3CN) [15,62]:

$$[Au^{III}(N_3)_4]^- \xrightarrow{h\nu} [Au^{I}(N_3)_2]^- + 3N_2 \qquad (17)$$

Azide radicals are observed as primary oxidation products of the azide ligands [70]. Initially, Au^{II} may be generated:

$$[Au^{III}(N_3)_4]^- \xrightarrow{h\nu} [Au^{II}(N_3)_3]^- + 1.5N_2 \qquad (18)$$

However, Au(Il) complexes are not very stable [71,72]. A further thermal reduction could take place:

$$[Au^{II}(N_3)_3] \rightarrow [Au^{I}(N_3)_2]^- + 1.5N_2 \qquad (19)$$

As an alternative, product formation can occur by a disproportionation:

$$2[Au^{II}(N_3)_3]^- \rightarrow [Au^{I}(N_3)_2]^- + [Au^{III}(N_3)_4]^- \qquad (20)$$

If the irradiation of $[Au(N_3)_4]^-$ is carried out with white light which includes the short-wavelength UV range $[Au^{I}(N_3)_2]^-$ undergoes a secondary photolysis ($\lambda_{irr} <$ 320 nm) as described above. It follows that in this case $[Au(N_3)_4]^-$ is completely converted to metallic gold [15]:

$$[Au^{III}(N_3)_4]^- \xrightarrow{h\nu} Au^0 + 4.5N_2 + N_3^- \qquad (21)$$

LMCT excitation of $[AuCl_4\ ]^-$ ($\lambda_{irr} > 250$ nm) or $[AuBr_4]^-$ ($\lambda_{irr} > 350$ nm) in ethanol leads also to a reductive elimination [30]. The concomitant spectral changes (Fig. 6) indicate the formation of $[Au^{I}X_2]^-$:

$$[Au^{III}X_4]^- \xrightarrow{h\nu} [Au^{I}X_2]^- + 2X \qquad (22)$$

Although the oxidation products were not identified the halogen atoms are assumed to be intercepted by the solvent, e.g.

$$2Cl + C_2H_5OH \rightarrow CH_3CHO + 2HCl \qquad (23)$$

Ethanol is a well-known reductant in photoredox reactions [73,74]. As described above the reductive elimination probably does not occur in one step but via the intermediate generation of Au(II).

As mentioned before the photosensitivity of solutions of Au(III) chloro complexes including Au(III) chloride has been known for centuries [2,3]. Generally, elemental Au was identified as final photoproduct. The photolyses were most efficient when reducing compounds were present. Unfortunately, much confusion exists with regard to the molecular mechanism of these photoreductions. According to our current knowledge the following processes seem to be involved. In the primary photochemical step Au(II) should be generated:

$$\mathrm{Au^{III}Cl_3 \xrightarrow{h\nu} Au^{II}Cl_2 + Cl} \tag{24}$$

In the presence of reducing agents chlorine atoms as well as Au(II) are reduced to chloride and AuCl. In the absence of electron donors a recombination competes with a disproportionation:

$$\mathrm{Au^{II}Cl_2 + Cl \rightarrow AuCl_3} \tag{25}$$

$$\mathrm{2AuCl_2 \rightarrow AuCl + AuCl_3} \tag{26}$$

Accordingly, the formation of AuCl is less efficient under these conditions. AuCl undergoes a further dispropoitionation in the absence of stabilizing ligands [14]. Final product formation proceeds then according to the equation:

$$\mathrm{3AuCl \rightarrow 2Au^0 + AuCl_3} \tag{27}$$

In the presence of reducing agents Au(I) can be also reduced photochemically in analogy to the secondary photolysis of $[\mathrm{Au(N_3)_4}]^-$ [15].

The irradiation of $\mathrm{Au^{III}(CH_3)_2}$(acetylacetonate) in organic solvents leads also to the deposition of elemental gold [75]. In addition, various organic products are formed which indicate the intermediate generation of methyl radicals. Accordingly, the photolysis may be induced by $\mathrm{CH_3^-} \rightarrow \mathrm{Au^{III}}$ LMCT excitation which should lead to the homolysis of the gold–carbon bond in the primary photochemical step. The resulting methyl radicals are very reactive and attack various substrates which are present including the solvent [76,77]. The primary photoreaction should lead to the

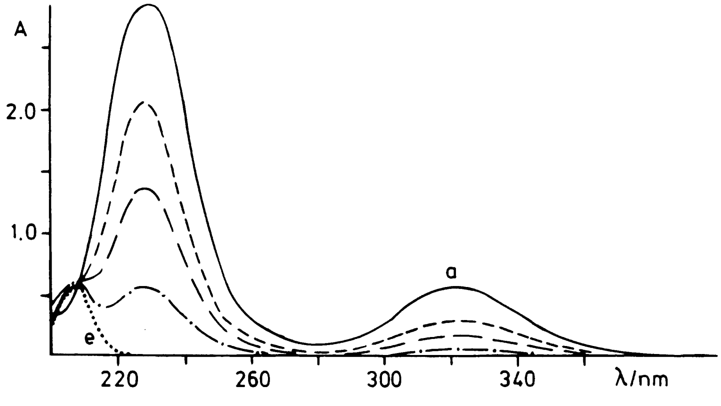
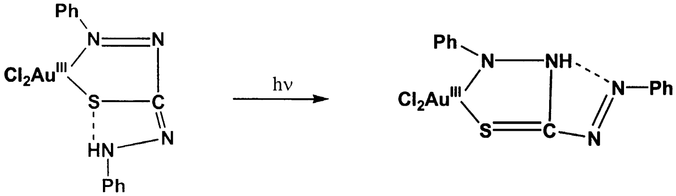


Fig. 6. Spectral changes during the photolysis of 6.34×10^{-5} M $[\mathrm{NBu_4}]\mathrm{AuCl_4}$ in ethanol at r.t. after 0 (a), 0.5, 1, 2 and 5 mm (e) irradiation time with $\lambda_{\mathrm{irr}} > 250$ nm, 1 cm cell.



Scheme 1.

formation of Au(II) which is subsequently reduced to Au(I) and finally to Au(0) as described above.

3.3.3. Ligand isomerization

IL excited states may be also reactive. Frequently, IL excitation is associated with ligand isomerizations [53]. This applies, for example, to dithizonate complexes [67,78]. The isomerization is accompanied by a color change. Generally, this isomerization is reversible and the complexes are thus photochromic. In the case of $Au^{III}(HDZ)Cl_2$ in $CHCl_3$ with $HDZ^- =$ dithizonate monoanion, the irradiation leads to an irreversible color change from violet to blue [67]. In analogy to other metal dithizonates [67,78] a photoisomerization of the dithizonate ligand may occur, see Scheme 1. However, the photolysis takes only place with UV light ($\lambda_{irr} < 400$ nm) while the IL bands appear in the visible spectral region ($\lambda_{max} = 540$ and 570 nm). Accordingly, a definite assignment of the reactive excited state is not yet possible.

Finally should be mentioned that Au(III) porphyrin complexes have been shown to participate in excited-state electron transfer processes [79,80]. However, the gold porphyrins function apparently as electron acceptors and their IL (porphyrin) excited states are not involved in these electron transfer reactions.

4. Conclusions

Complexes of Au in its common oxidation states I and III are frequently light sensitive. The reactive excited states are of the MC (dd, ds), LMCT, MLCT, MMCT and IL type. In many cases the photolysis leads finally to the deposition of metallic gold but there are indications that these photoreactions proceed by a complicated mechanism.

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