Electronic Spectra of Bis(dihydrogen tellurato) and Bis(hydrogen periodato) Complexes of Copper(III), Silver(III) and Gold(III)

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The electronic spectra of bis(dihydrogen tellurato) and bis(hydrogen periodato) complexes of copper-(III), silver(III) and gold(III) have been studied. Three intense bands for $[M(HIO_6)_2]^{5-}$ (M = Cu(III), Ag-(III)), two bands for $[M(H_2TeO_6)_2]^{5-}$ (M = Cu(III), Ag(III)) and one band for $[Au(H_2TeO_6)_2]^{5-}$ and $[Au(HIO_6)_2]^{5-}$ were identified by means of gaussian analysis of the experimental spectra. All these bands have been attributed to Ligand → Metal charge transfer transitions. The ligand field bands (d–d transitions) were not found in this study.

Introduction

The spectroscopic properties of copper(III), silver(III) and gold(III) ions co-ordinated to ligands such as tellurate and periodate have received little attention [1–5]. Not much has been done on the overall optical properties of these complexes. L. Jensovsky [1] has studied the bis(tellurato) and bis-(periodato) complexes of copper(III) and silver(III). He observed two bands which he attributed as due to charge transfer of the type Ligand → Metal (L → M) and the third band at 334 nm (ϵ = 2500 M^{-1} cm^{-1}) and at 312 nm (1800 M^{-1} cm^{-1}) for the bis(periodato)cuprate(III) and bis(periodato)argentate(III) respectively was attributed as arising from the products resulting from the decomposition of these complexes. A very weak band at 560 nm with much uncertainty was also observed for the bis(periodato)-cuprate(III).

The UV–visible spectral studies of the periodato complexes of copper(III), silver(III) and gold(III) by R. Pappalardo *et al.* [2] showed two bands for the complexes of Cu(III) and Ag(III) with doubts cast on the second band at 40000 cm^{-1} observed for the copper complex. Only one band at 37880 cm^{-1} was observed for gold(III) periodato complex ion in aqueous solution. These complexes were treated by the authors as being square-planar; the intense bands observed was described by them as due to L → M charge transfer transition. The first band for the periodato complexes of copper(III), silver(III) and

gold(III) was attributed to the transition $\pi \rightarrow \gamma t_3$-($d_{x^2-y^2}$). The second, absent on the case of gold(III), was attributed to the $\sigma \rightarrow \gamma t_3$ transition. K. B. Yatsi-mirskii *et al.* [3] studied the spectra of copper(III) periodato complex in the range 10000–33000 cm^{-1} and observed three bands. The first band at 18500 cm^{-1} (ϵ = 250 M^{-1} cm^{-1}) was attributed to the d–d transition while the two others at 24100 cm^{-1} (ϵ = 11100 M^{-1} cm^{-1}) and 27300 cm^{-1} (ϵ = 4590 M^{-1} cm^{-1}) were attributed to L → M charge transfer. These authors assumed the ligand field arising from the periodato ion as being octahedral and they assigned the d–d transition as being that of $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$. This observation contradicts the observation of the authors cited above and also that of G. L. Cohen and G. Atkinson [4]. A study of the magnetic properties of periodato and tellurato complexes of Cu(III), Ag(III) and Au(III) has shown that these complexes are diamagnetic and the ground state of these complexes cannot be $^3A_{2g}$ as assumed by K. B. Yatsimirskii. Furthermore these complexes have been shown to be tetragonal [4, 8], in agreement with the low spin (S = O) d^8 system of which the most characteristic ions are Ni(II) Pd(II), Pt(II) and Au-(III) [9].

G. L. Cohen *et al.* [3] observed 3 absorption maxima at 216 nm (ϵ = 1.5 X 10^4 M^{-1} cm^{-1}), 255 nm (ϵ = 1.45 X 10^4 M^{-1} cm^{-1} and 362 nm (ϵ = 1.4 X 10^4 M^{-1} cm^{-1}) for bis(periodato)argentate(III) in aqueous solution. These were attributed to charge transfer bands because of their high extinction coefficients.

In addition to the incomplete spectral studies performed on these complexes and the lack of agreement as to the position of bands, there is also disagreement on the interpretation of these bands. In our previous report [5] a brief account of the spectral studies of bis(dihydrogen tellurato) and bis-(hydrogen periodato) complexes of copper(III) and silver(III) was given. These studies showed that the spectra of these complexes are sensitive to temperature. A detailed UV–visible spectral study of these complexes in aqueous solution has been attempted. In order to interpret the spectra quantitatively the
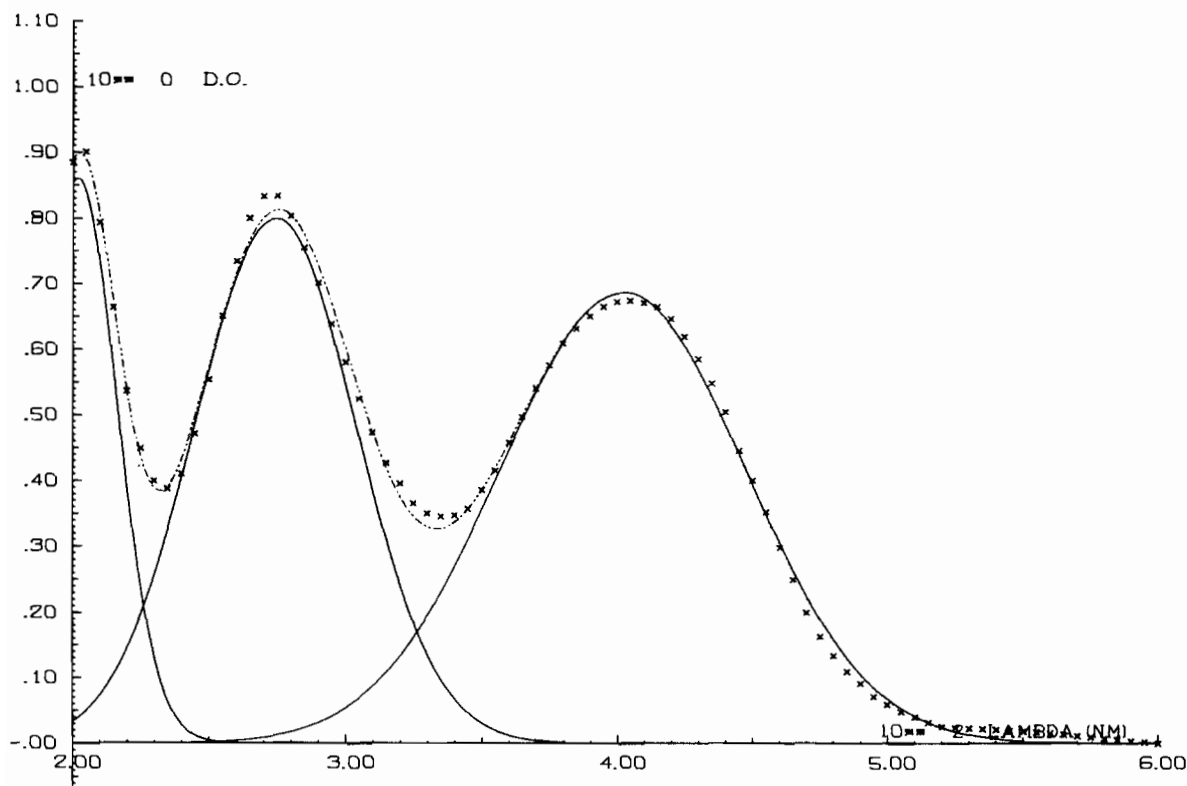
Figure 1. U.V.–visible spectrum of bis(dihydrogen tellurato)cuprate(III). These symbols: (———) gaussian components; (·····) sum of the gaussian components; (×××) experimental spectra, have been used for all the spectra.

Experimental

position of the absorption maximum, the molar extinction coefficient and the oscillator strength were determined by carrying out gaussian analyses of these curves.

The complexes bis(dihydrogen tellurato) and bis(hydrogen periodato)cuprate(III) and argentate-(III) were synthesised as described previously [5]. The gold analogue was synthesised as described in our previous report [10]. In order to completely remove impurities from the synthesised complexes, these complexes were recrystallised as described in earlier papers [5, 10]. Since $[Cu(H_2TeO_6)_2]^{5-}$ and $[Cu(HIO_6)_2]^{5-}$ decomposed during recristallisation the crude complex was used for spectral studies. As these complexes were sufficiently pure, it was not absolutely essential to recrystallise these compounds.

The aqueous solutions of all the complexes were made by dissolving the complexes in demineralized water which was boiled first and then cooled to 3.0 ± 0.5 °C. The spectra were run at this temperature.

A comparative study of the influence of temperature and irradiation (406 and 277 nm) on the spectra of aqueous solutions of $[Cu(H_2TeO_6)_2]^{5-}$ showed that if measurements are carried out in closed cells

then the temperature is the chief source of decomposition of the complex [11]. We observed that the optical density at 406 nm after 1 h decreased by ca. 32 ± 1% at 26 °C, 22 ± 1% at 23 °C and 8 ± 1% at 10 °C. The copper(III) complex was chosen as an example because the stability of these complexes varies in the order Cu(III) < Ag(III) < Au(III) [2].

The spectra were recorded on a DB-G spectrophotometer coupled to a Hi-speed 202 recorder. The solutions were put in closed quartz cells (1 cm). The concentrations of the solutions were determined by measuring the concentration of the central metal atom by means of atomic absorption spectrophotometry (A.A.S). A Pye Unicam SP 1900 spectrophotometer was used for this purpose.

The gaussian curve for the spectra and computations of λ_{max}, ϵ_{max} and f for the individual bands were done by means of a UNIVAC 1108 computer connected to a Benson 1251 plotter (University of Geneva).

Results and Discussion

In general any absorption spectrum can be approximated to a gaussian function. Several expressions to describe the exact form of the band have been proposed [12, 13]. The gaussian expression used in this work was
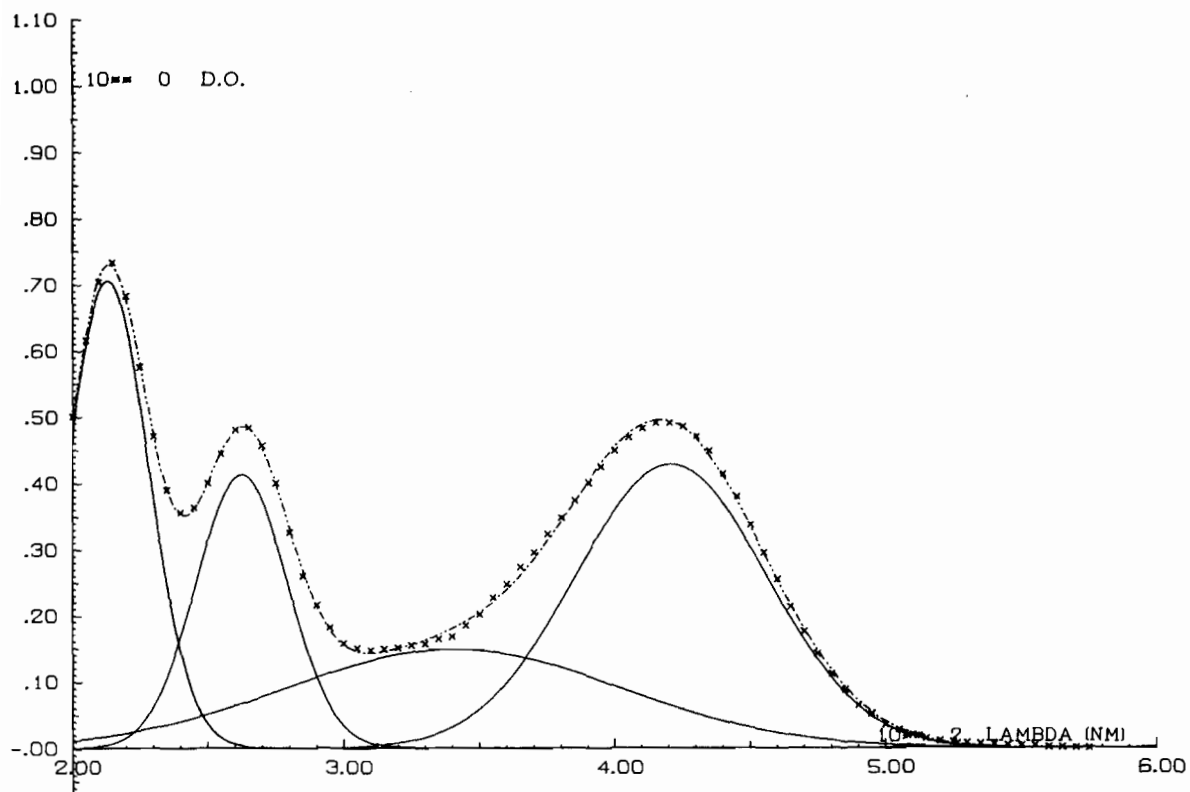
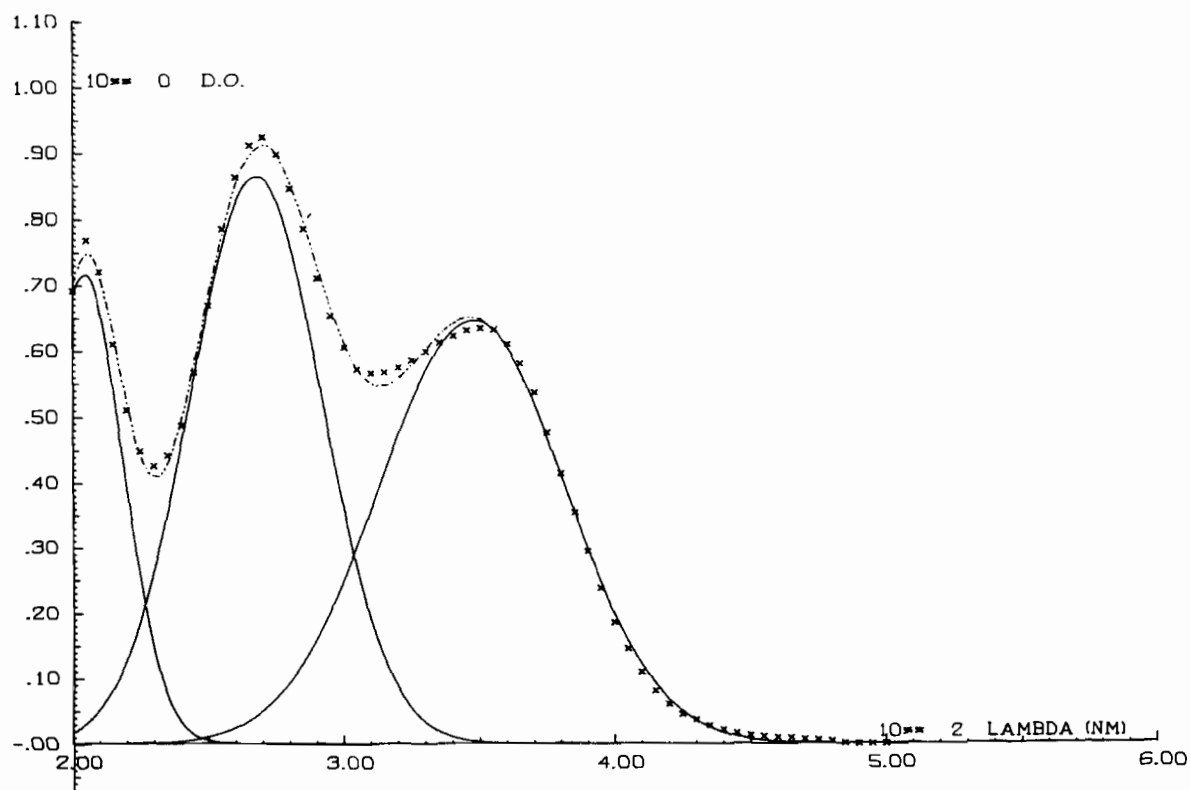Figure 2. U.V.–visible spectrum of bis(hydrogen periodato)cuprate(III).

Figure 3. U.V.–visible spectrum of bis(dihydrogen tellurato)argentate(III).
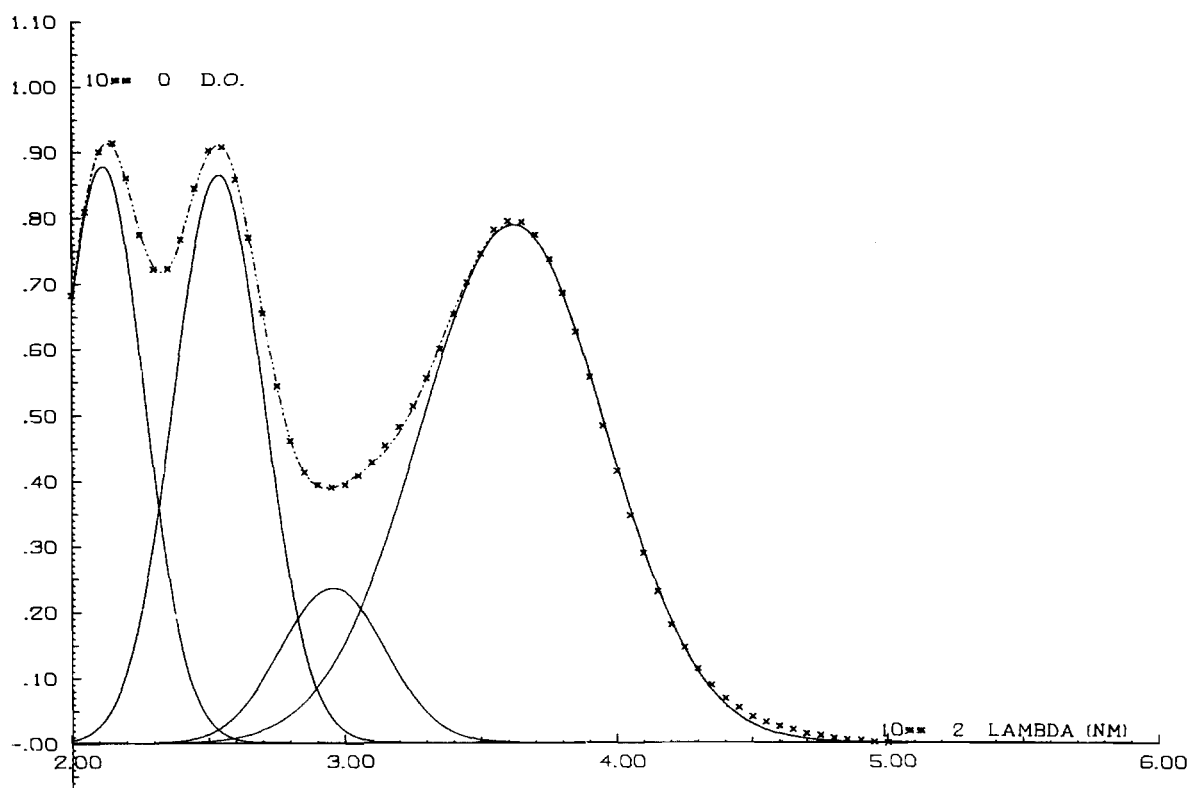
Figure 4. U.V.–visible spectrum of bis(hydrogen periodato)argentate(III).

$$\epsilon = \epsilon_{max} e^{-(\nu - \nu\ max)^2 \theta^{-2}}$$

where ϵ = molar extinction coefficient

ν = wavenumber

θ = half-width of the band at half the peak height

The oscillator strength, f, was calculated by using f = $4.60 \times 10^{-9}\ \epsilon_{max}\ \delta(\delta = 2\theta$, in cm^{-1}). A computer program written by Beech [13] was used for resolving the spectra into gaussian curves. This program was modified to fit with our experimental conditions. The spectra thus obtained are given in Figs. 1–6, where optical density instead of extinction coefficient is plotted against wavelength. The full lines in the figures represent gaussian components, the broken lines show the sum of the gaussian curves and crosses represent the experimental curve. It can be seen from these figures that the curves constructed from the gaussian expression (-·-·-) are in fair agreement with the experimental curve (XXX). All the complexes studied exhibit a band at 208 nm. This can be attributed to intra-ligand transition. In fact when periodate or tellurate solution is used as a blank this band disappears. Moreover spectrochemical studies have shown that periodate solutions absorb at *ca.* 220 nm [14]. The shift of the bands towards higher energies may be due to the influence of central metal atom. Hereafter this band will not be considered for further discussion. The parameters

characteristic of each band are summarised in the Table given on page 145.

The magnitude of the molar extinction coefficients and the oscillator strength values seem to indicate that the transitions are allowed ones. However, previous interpretations [1–4] suggest that there is L → M charge transfer transition at least in the case of highly intense bands.

From purely electrostatic considerations, the energy ΔE due to electron transfer from ligand to the central metal M^{n+} and the nth ionisation potential, I_n [15], are related by the following expression:

$$\Delta E = -I_n + E_L + \Delta M$$

where E_L is the electron affinity of the ligand and ΔM is the change in Madelung, polarisation and related energies. The third ionisation potential of Cu(III), Ag(III) and Au(III) are 37.079, 34.818 and 30 eV respectively [16]. The position of the first band for $[Cu(H_2TeO_6)_2]^{5-}$, $[Au(H_2TeO_6)_2]^{5-}$, and $[Au(H_2TeO_6)]^{5-}$ are at 24.88, 28.83 and 40.82kK respectively. For $[Cu(HIO_6)_2]^{5-}$, $[Ag(HIO_6)_2]^{5-}$ and $[Au(HIO_6)_2]^{5-}$ the band appears at 23.75, 27.62 and 41.15kK respectively. The experimental value of ΔE as a function of I_n (n = 3) is shown in Fig. 7a for bis(dihydrogen tellurato) complexes and in Fig. 7b for bis(hydrogen periodato) complexes. The same trend was also observed for other bands. The linear relationship obtained for $\Delta E = f(I_n)$ clearly shows

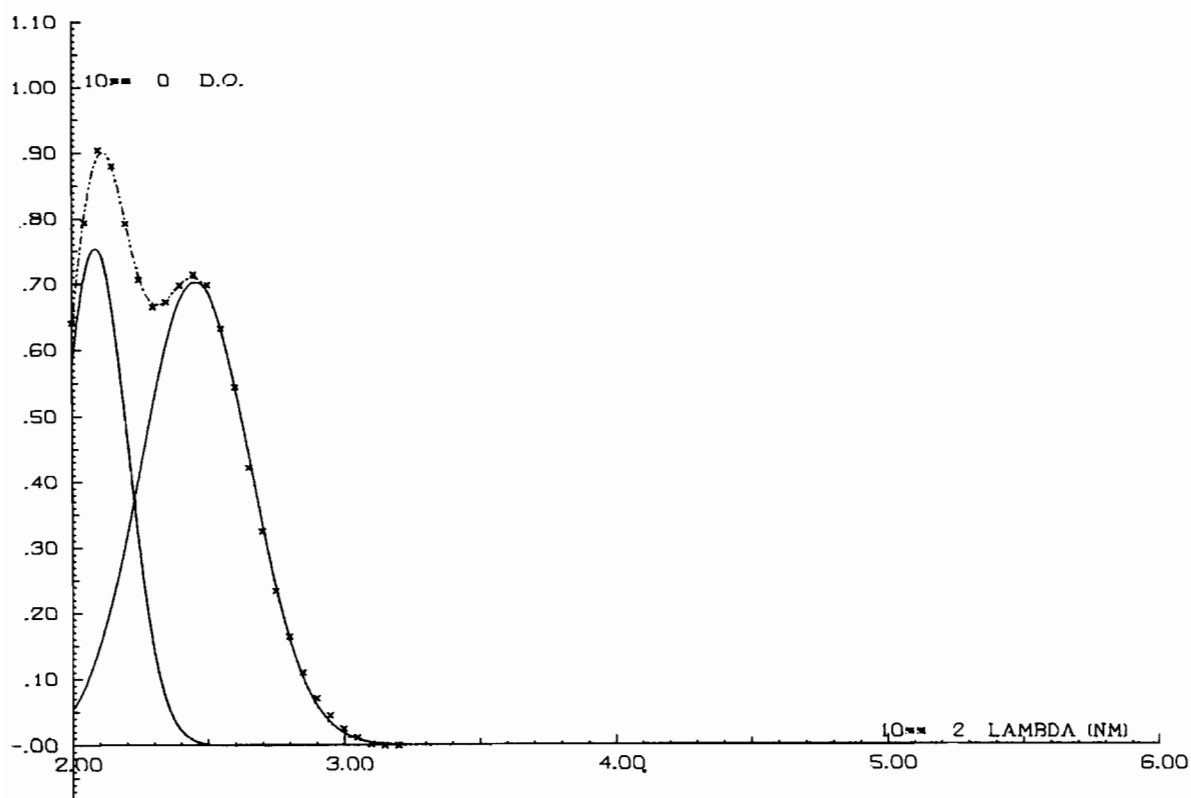| Complex	λ (nm)	$\nu = \Delta E$ (kK)	ϵ_{max} (M^{-1} cm^{-1})	f
$[Cu(H_2TeO_6)_2]^{5-}$	402	24.88	7368	0.278
	274	36.50	8552	0.448
$[Cu(HIO_6)_2]^{5-}$	421	23.75	9028	0.239
	340	29.41	3134	0.235
	262	38.17	8720	0.277
$[Ag(H_2TeO_6)_2]^{5-}$	347	28.82	9307	0.352
	267	37.45	12962	0.562
$[Ag(HIO_6)_2]^{5-}$	362	27.62	12592	0.435
	295	33.90	3766	0.109
	254	39.37	13815	0.466
$[Au(H_2TeO_6)_2]^{5-}$	245	40.82	12541	0.551
$[Au(HIO_6)_2]^{5-}$	243	41.15	17769	1.08

Figure 5. U.V.–visible spectrum of bis(dihydrogen tellurato)aurate(III).

that these bands are due to L → M type charge transfer. Ligand field transition was not observed in our case. However, R. S. Banerjee and Basu [17] claim that three bands at 425, 445 and 475 nm are observed in addition to the intense bands for $[Cu(H_2TeO_6)_2]^{5-}$. They obtained these bands by gaussian analyses of the spectra. An analogous band with some doubt has been reported by L. Jensovsky [1] at 560 nm (ϵ = 500 M^{-1} cm^{-1}) but K. B. Yatsimirskii

et al. [3] claim the same band to be at 540 nm (ϵ = 250 M^{-1} cm^{-1}). These results indicate that it is extremely difficult to identify weak bands by gaussian analysis. Furthermore by carrying out such analysis of the spectra of these compounds, we did not find such bands.

As d^8 low spin (S = 0) compounds are generally square planar, Cu(III), Ag(III) and Au(III) complexes with d^8 electrons and diamagnetic would be
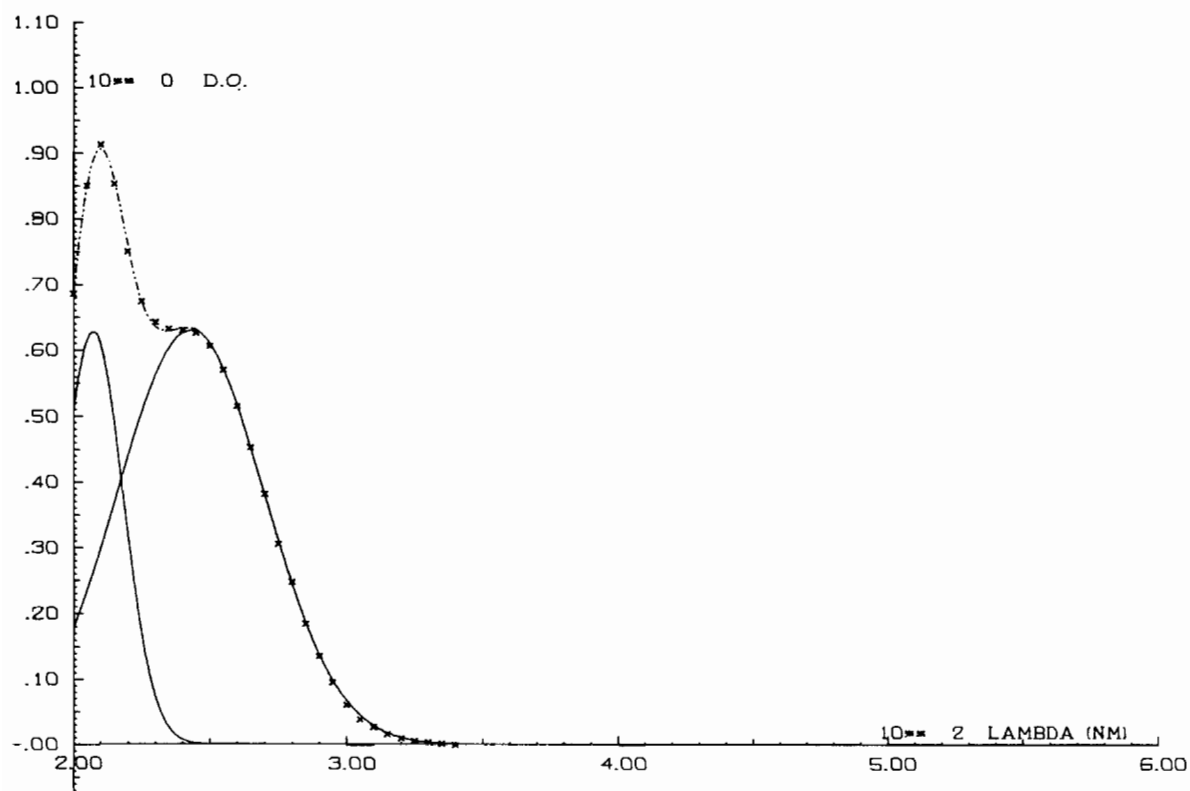
Figure 6. U.V.–visible spectrum of bis(hydrogen periodato)aurate(III).

expected to have a D_{4h} (square planar) or D_{2h} (rectangular) symmetry. Copper(III), silver(III) and gold(III) ions form tetra co-ordinated bonds with oxygen atoms of the bidentate tellurate and periodate. For simplicity this bonding will be written as MO_4. The absorption spectra of d^8 low spin (S = 0) tetra co-ordinated dithio complexes of Ni(II), Pd(II), Pt(II) and Au(III) [18–23] have been extensively studied and these complexes MS_4 (M = Ni(II), Pd(II), Pt(II) and Au(III)) have been assigned D_{2h} point group. Thus it is reasonable to assume that MO_4 (M = Cu(III), Au(III) and Ag(III)) will have analogous structure and will belong to D_{2h} point group. The ligand orbitals of σ character are a_g, b_{1g}, b_{2u} and b_{3u} whereas the π type $(\pi_v + \pi_h)$ are a_g, a_u, b_{1g}, b_{1u} b_{2u}, b_{3g} and b_{3u} [18–23]. Although there is no consensus of opinion as to the order of the energy levels of these orbitals in D_{2h} symmetry, one point about which there is no doubt is that the vacant orbital is $b_{1g}(d_{xy})$ and the highest filled orbital is $a_g(d_{x^2-y^2})$.

In our opinion the complexes of the type MO_4 studied at present fit with the MS_4 model and the interpretation of our spectra is based on this assumption.

The ground state of the group of complexes of the type MO_4 (d^8 S = 0) in D_{2h} symmetry is......$(a_g)^2$: ^1A_g. The transitions which are allowed are between
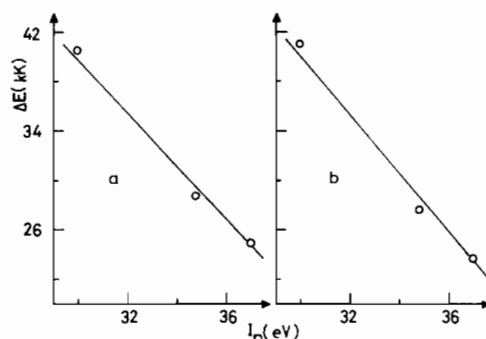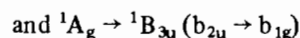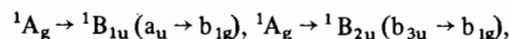

Figure 7. The maximum of the first charge-transfer band $\Delta E(kK)$ *vs.* the 3rd ionisation potential I_3 (eV) of M^{3+} (M = Cu, Ag, Au); a) dihydrogen tellurato complexes; b): hydrogen periodato complexes.

the orbitals essentially localised on the ligand and the vacant orbital b_{1g} (d_{xy}). For the D_{2h} point group, the allowed transitions are as follows:

$$^1A_g \rightarrow {}^1B_{1u}(a_u \rightarrow b_{1g}), \quad {}^1A_g \rightarrow {}^1B_{2u}(b_{3u} \rightarrow b_{1g}),$$

$$\text{and } {}^1A_g \rightarrow {}^1B_{3u}(b_{2u} \rightarrow b_{1g})$$

Theoretical studies on the complexes of the type MS_4 in D_{2h} symmetry have shown that ligand π orbitals, $L(\pi)$:2 b_{2u} and 2 b_{3u} are degenerate and ligand σ orbitals, $L(\sigma)$:1 b_{2u} and 1 b_{3u} are also

degenerate. There is still some doubt about the energy of the $a_u(\pi)$ [18, 19, 20, 22]. H. B. Gray [18] has pointed out that MS_4 complexes should give two charge transfer bands L → M arising from $L(\pi) → b_{1g}$ (d_{xy}) and $L(\sigma) → b_{1g}$ transitions with an interval of 10000 cm^{-1} between them. Two bands at 402 and 274 nm were observed for $[Cu(H_2TeO_6)_2]^{5-}$ (Fig. 5), the intervals between these bands being 11620 cm^{-1}. Two bands at 347 and 267 nm and 8635 cm^{-1} apart were observed for $[Ag(H_2TeO_6)_2]^{5-}$ (Fig. 3). Thus these results show clearly that the observed bands are due to charge transfer from L → M. The bands at 402 and 347 nm observed for $[Cu(H_2TeO_6)_2]^{5-}$ and $[Ag(H_2TeO_6)_2]^{5-}$ respectively can be attributed to $^1A_g → {}^1B_{3u}, {}^1B_{2u}$ (2 b_{2u}, 2 $b_{3u} → b_{1g}$). The bands at 274 and 267 nm for these complexes can be attributed to $^1A_g → {}^1B_{3u}. {}^1B_{2u}$ (1 b_{2u}, 1 $b_{3u} → b_{1g}$). L. Jensovsky reports two bands for copper(III) analogue and only one band for the silver complex. The position of these bands is in agreement with those observed by us except that their molar extinction coefficients are 15–22% lower than ours. Since the complexes are sensitive to temperature changes and atmospheric CO_2, the differences in molar extinction coefficient may arise from these factors. The band at 267 nm ($\epsilon = 12962$ M^{-1} cm^{-1}) for $[Ag(H_2TeO_6)_2]^{5-}$ (Fig. 3) was absent in Jensovsky's spectrum. In fact we found that if the complexes were not recrystallised, then the spectra of the aqueous solution give an increasing absorbance below $\lambda = 340$ nm thus obscuring the band at 267 nm.

The anions $[Cu(HIO_6)_2]^{5-}$ and $[Ag(HIO_6)_2]^{5-}$ exhibited 3 bands with two intense ones at 421 and 262 nm (Fig. 2) for the copper complex and at 362 and 254 nm for the silver analogue. These bands were 14415 cm^{-1} and 11745 cm^{-1} apart for the copper and silver complex respectively. The bands at 421 and 362 nm for the copper(III) and silver(III) complexes respectively can be attributed to $^1A_g → {}^1B_{3u}$, $^1B_{2u}$(2 b_{2u}, 2 $b_{3u} → b_{1g}$) transitions whereas the bands at 262 and 254 nm for these complexes are due to $^1A_g → {}^1B_{3u}, {}^1B_{2u}$ (1 b_{2u}, 1 $b_{3u} → b_{1g}$) transitions. There is an agreement between results obtained by various authors regarding the position of the bands for $[Cu(HIO_6)_2]^{5-}$ complex but as regards the intensity of these bands there is no agreement whatever. The band corresponding to 421 nm (Fig. 2) with $\epsilon = 9029$ M^{-1} cm^{-1} has been observed at 415 nm by some workers in this field [1–3]. The molar extinction coefficient for this band has been quoted as $\epsilon = 11800$ M^{-1} cm^{-1} [1], $\epsilon = 2400$ M^{-1} cm^{-1} [2] and $\epsilon = 11000$ M^{-1} cm^{-1} [3]. The second band at 262 nm ($\epsilon = 8720$ M^{-1} cm^{-1}) observed by us was identified at 265 nm ($\epsilon = 11400$ M^{-1} cm^{-1}) by Jensovsky [1]. The other workers did not determine the extinction coefficient for this band. The intensities of these two bands are approximately the same with the band in the visible being slightly more intense than that in the UV, in accord with the observations made by Jensovsky [1]. There is however a difference of *ca.* 23% in molar extinction coefficient values between the above author's values and ours. In order to avoid difficulties due to thermal decomposition and atmospheric CO_2 on the complex, experiments were done in a closed cell and at 3.0 ± 0.5 °C. The results thus obtained for the molar extinction coefficients were reproducible. On the other hand, gaussian analysis shows a broad band $(\delta = 2\theta = 176$ nm) at about 340 nm (Fig. 2). This band has an appreciable influence on the bands at 421 and 265 nm. In fact the difference between the gaussian components and experimental curve at the absorption maximum is *ca.* 15%. Such a band has also been reported by Jensovsky [1]. However, according to the author's gaussian analysis, this band does not have any effect on the bands near 415 and 265 nm. Furthermore the author did not take into account the bands found in the far ultraviolet region for the gaussian analysis. If this were the cause for the observed differences between his and our results, it still does not completely account for a difference of 23% in the intensities. The only explanation for this discrepancy is the effect of CO_2 and the thermal decomposition of the complex during optical studies and chemical analysis.

The results obtained with $[Ag(HIO_6)_2]^{5-}$ are analogous to those of the copper analogue except that the differences between Jensovsky's results [1] and ours are less marked than in the case of copper. The first band was observed at 362 nm ($\epsilon = 12592$ M^{-1} cm^{-1}), the same band was observed at 366 nm ($\epsilon = 14600$ M^{-1} cm^{-1}) by Jensovsky [1]. Pappalardo *et al.* [2] observed it at 362 nm (ϵ was not given) whereas G. L. Cohen *et al.* [4] found $\epsilon = 14000$ M^{-1} cm^{-1} at 362 nm. There is a general agreement with regard to the position of the very intense band found in the UV [2, 4, 5] with the exception of Jensovsky [1] who reports this band at 244 nm. The same phenomenon which seems to be an artifact was observed by us and results from the presence of large excess of periodate present in the solution containing the complex. The band due to periodate at 215 nm is so intense that it obscures the band due to the complex at 254 nm. However, this effect was overcome by recrystallising the complex. The values of ϵ calculated by us were *ca.* 5–10% lower than those determined by G. L. Cohen *et al.* [4]. This difference may be due to the precision with which the concentration of the complex is measured. This was done by A.A.S. by us whereas G. L. Cohen *et al.* [4] used the gravimetric method. Moreover, these authors have not corrected the partially overlapping band which they observe at 215 nm; we found the corresponding band at 211 nm (Fig. 4).

The bands determined by gaussian analysis for $[Cu(HIO_6)_2]^{5-}$ and $[Ag(HIO_6)_2]^{5-}$ at 340 and 295

nm respectively were reported at 334 nm and 312 by Jensovsky [1]. According to Jensovsky these bands arise from the decomposition of the complex. However we fail to see how the products of decomposition of these complexes have such high intensities especially in this region of wavelength since it is known that periodates absorb at 220 nm [14]. In our opinion these bands are related to the nature of these complexes. The fact that their intensities are $\epsilon = 3134 \ M^{-1} \ cm^{-1}$ at 340 nm for $[Cu(HIO_6)_2]^{5-}$ and $\epsilon = 3766 \ M^{-1} \ cm^{-1}$ at 295 nm for $[Ag(HIO_6)_2]^{5-}$; the molar extinction coefficient values, the oscillator strength and their relative positions seem to indicate that these absorptions are allowed by the selection rules and that they can be grouped together in the L → M type charge transfer bands. Thus these bands can be attributed to $^1A_g \rightarrow {}^1B_{1u}$ ($a_u \rightarrow b_{1g}$) transition. Nevertheless, the width of the band for copper complex ($\delta = 176$ nm) is rather surprising. Although the reason for this is unknown at present, the bands were found to be reproducible for this complex suggesting that it cannot be an artifact.

The question that comes to mind is why such a band is not observed with bis(dihydrogen tellurato)-cuprate(III) and argentate(III). Theoretical studies of the energy levels of the molecular orbitals of MS_4 type complexes having D_{2h} symmetry predict that in general the $a_u(\pi)$ level is below the $L(\sigma)$ orbitals ($1 \ b_{2u}$, $1 \ b_{3u}$) [18, 20, 22]. In some cases however the $a_u(\pi)$ orbital either lies between $L(\sigma)$ and $L(\pi)$ [20] or is at the same energy level as $L(\pi)$. According to Latham *et al.* [19] when $a_u(\pi)$ orbital is at the same energy level as $2 \ b_{2u}$ and $2 \ b_{3u}$, then the $L(\pi) \rightarrow b_{1g}(d_{xy})$ transition will be stronger than $L(\sigma) \rightarrow b_{1g}$ as is observed for nickel(II) dithiooxalate, although generally the reverse is observed with other complexes. Thus in the case of $[Cu(H_2TeO_6)_2]^{5-}$ and $[Ag(H_2TeO_6)_2]^{5-}$ the $a_u(\pi)$ is at a lower energy level than $L(\sigma)$ and this band is not observed. But in the case of $[Cu(HIO_6)_2]^{5-}$ and $[Ag(HIO_6)_2]^{5-}$, the $a_u(\pi)$ level lies between $L(\sigma)$ and $L(\pi)$.

In the case of gold(III) complexes an intense band at 245 nm ($\epsilon = 12541 \ M^{-1} \ cm^{-1}$) for $[Au(H_2TeO_6)_2]^{5-}$ (Fig. 5) and at 243 nm ($\epsilon = 17769 \ M^{-1} \ cm^{-1}$) for $[Au(HIO_6)_2]^{5-}$ (Fig. 6) was observed. For the latter complex Pappalardo and Losi [2] have reported a band at 37880 cm^{-1} *i.e.* 260 nm ($\epsilon = 26000 \ M^{-1} \ cm^{-1}$) which is different from our results. The reason for this is not clear at present. The gaussian analysis of the curve enabled us to resolve this band from the band due to localised intra-ligand

transition at 209 nm for the tellurate and at 207 for the periodate complexes. The single band for these complexes around 245 and 243 nm may be attributed to $^1A_g \rightarrow {}^1B_{3u}$, $1B_{2u}$ ($2 \ b_{2u}$, $2b_{3u} \rightarrow b_{1g}$) transitions. It is reasonable to expect only one band due to charge transfer since the second band ($L(\sigma) \rightarrow b_{1g}$) will be expected at 190 nm.

Acknowledgment

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