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Studies of the Coordination Complexes of Bis(dihydrogen tellurato) and Bis(hydrogen Periodato)Aurate(III)

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The complexes ditellurato- and diperiodato-aurate(III) were prepared and studied by analytical, infra-red and conductimetric methods. The results show the protonation of these complexes and allow a determination of the anionic charge. The constitutions proposed for the two ions are $[Au(H_2TeO_6)_2]^{5-}$ *and* $[Au(HIO_6)_2]^{5-}$.

Introduction

The periodate and tellurate complexes of Au(III), unlike their Cu(III) and Ag(III) analogues, have not received much attention. Studies on the nature of $H_2Na_5[Au(IO_6)_2]\cdot17H_2O$ [1] and $H_3Na_6[Au(TeO_6)_2]\cdot14H_2O$ [2], and the optical properties of complexes of the type $Na_xH_y[M(IO_6)_2]\cdot nH_2O$ [3] ($x + y = 7$, M = Cu(III), Ag(III) or Au(III)), have been reported.

In our previous work [4], we showed that tellurate and periodate complexes occur as $[M(HIO_6)_2]Na_5\cdot nH_2O$ and $[M(H_2TeO_6)_2]Na_5\cdot nH_2O$ (M = Cu(III) or Ag(III)), n varying from one synthesis to another. It is thus of interest to know whether the periodate and tellurate of gold also show the same characteristics, in particular if the ligands are in the protonated form, and if so, the extent of protonation and the charge of the anionic complex.

Experimental

Synthesis of Ditellurato- and Diperiodato-aurate(III)

Ditellurato-aurate(III)

K_2TeO_4 (2 g), KOH (3 g) and demineralised water (100 ml) were added to $HAuCl_4$ (1 g), and the mixture was heated until all the solid dissolved. The resulting solution was initially bright yellow but gradually turned pale yellow. After allowing the pale yellow solution to stand for two hours, K_2TeO_4 (1 g dissolved in minimum amount of water) was added to it. The resulting solution became colourless after three hours. Small amounts of brown suspension was observed, presumably due to the formation of gold colloid, and it was filtered off. 50% $NaNO_3$ (40 ml) was added to the filtrate and the mixture was left to crystallise (*ca.* 12 hours). When white flakes were obtained, this was dissolved in minimum amount of dilute alkali solution (KOH, pH ~12) and recrystallised from 50% $NaNO_3$ solution (20 ml) at room temperature. The white crystals thus obtained were washed with water and dried *in vacuo.*

Diperiodato-aurate(III)

The same procedure as described above was used for preparing this complex. Reagents used for this purpose were $HAuCl_4$ (1 g), KOH (3 g), and KIO_4 (3.5 g). The product was recrystallised as described previously for diperiodato-argentate(III) [4]. Pale yellow crystals were obtained.

Analysis of the Complexes

In order to determine the stoichiometry of the complexes prepared, elemental analysis of the compounds was carried out. Gold was determined by atomic absorption spectrometry (A.A.S.) whereas potassium and sodium were analysed by flame photometry. A.A.S. Pye Unicam SP 1900 was used for this purpose. $Te(VI)O_6$ was determined by differential pulse polarography by means of PAR (electrochemistry system 170). For comparison purposes, Te was also determined by A.A.S. The results obtained by both these methods were in good agreement with each other and because of the simplicity and rapidity of A.A.S., this method was used for all Te analyses. $I(VII)O_6$ was determined by reducing it with ascorbic acid, but as Au(III) is also reduced to Au(0), excess ascorbic acid was added and back titrated with I_2. As the gold content has already been determined, the amount of ascorbic acid oxidised by the gold is known, and the amount oxidised by the $I(VII)O_6$ group may be calculated by subtraction. Water of crystallisation was determined by thermogravimetry using Mettler analyser T.A.1. The results of all these analyses are given in Table I.

From these results, the following stoichiometric composition for the anionic group was obtained: Au:

TABLE I. Analyses of the Complexes.

Ditellurato-aurate(III)

Element	Au	TeO_6	Na	K	H_2O
% Composition	18.72	49.54	10.78	–	20.09
Molar Ratio	1	: 2.33	: 4.94	: –	: 11.75

Diperiodato-aurate(III)

Element	Au	IO_6	Na	K	H_2O
% Composition	21.80	54.23	12.84	0.05	6.96
Molar Ratio	1	: 2.20	: 5.05	: 0.01	: 3.49

$TeO_6(IO_6)$: Na = 1:2:5. The sum of the percentages for ditellurato-aurate(III) was found to be 99%, which is satisfactory considering the experimental error inherent to each method. However, the added percentage composition found for diperiodato-aurate(III) was 96%, which is rather low. This discrepancy stems from the inaccuracy in thermogravimetric analysis of water. The base line of the thermogram for water is ill-defined, as was also observed with Cu(III) and Ag(III) analogues [4]. Attempts to get better results using G. L. Cohen *et al.* 's method [5] were unsuccessful. The Karl–Fischer method for water analysis being inadequate in this case, the results obtained by thermogravimetric method were retained.

The molar ratio found for diperiodato-aurate(III) was in accordance with those previously reported [1], but ditellurato-aurate(III) gave a 1:2:5 ratio for Au:TeO_6:Na instead of 1:2:6 [2]. Cu(III) and Ag(III) analogues gave the same results [4] thus confirming that in tellurate complexes the M:TeO_6:Na ratio is 1:2:5 (M = Cu, Ag or Au). The high value for sodium found previously [2] is due to the difficulty in analysing this element.

I.R. Spectra of Ditellurato and Diperiodato Complexes of Au(III)

Since the identification of Te–OH and I–OH bonds in Cu(III) and Ag(III) analogues [4] was made possible by running I.R. spectra, the I.R. spectra of gold complexes were also run for the same purpose. The samples were prepared as described previously [4] and spectra were recorded on a Perkin–Elmer 357 spectrophotometer.

Results and Discussion

Ditellurato-aurate(III)

The I.R. spectrum of ditellurato-aurate(III) (Fig. 1a) was interpreted by comparing the work of H. Siebert [6] on telluric acid (H_6TeO_6), sodium orthotellurate ($Na_2H_4TeO_6$), and potassium orthotellurate trihydrate ($K_2H_4TeO_6 \cdot 3H_2O$). An intense, broad band between 2500 and 3700 cm^{-1} shown in Fig. 1a, consists of stretching frequency for OH group of water at 3400 cm^{-1}, while the band at *ca.* 3000 cm^{-1} corresponds to the OH stretching mode for the TeOH group. The latter band is not very distinct, due to the presence of water of crystallisation in the complex (20.09%). The band at 2230 cm^{-1} corresponds to overtones or a combination band of the TeOH bending modes observed at 1150 and 1250 cm^{-1} as reported by Siebert [6]. Two fairly strong bands are observed at 1600 cm^{-1} and 1440 cm^{-1} (Fig. 1a). These bands were absent in orthotelluric acid [4, 6], but present in potassium orthotellurate trihydrate (*ca.* 1630 and 1490 cm^{-1}), which were attributed to OH bending mode arising from H_2O molecules. H. Siebert observed two bands at 1141 and 1200 cm^{-1} for sodium orthotellurate, three bands at 1125, 1119 and 1222 cm^{-1} for orthotelluric acid, one band at 1095 cm^{-1} for $K_2H_4TeO_6 \cdot 3H_2O$. The band at *ca.* 1100 ± 100 cm^{-1} was attributed to the TeOH bending mode (δ TeOH) by the author. In the case of ditellurato-aurate(III) (Fig. 1a), two bands were observed at 1100 and 1200 cm^{-1} and can be attributed to TeOH bending mode (δ TeOH). The compounds studied by H. Siebert [6] gave several bands between 800 and 600 cm^{-1} which the author attributed to the Te–O stretching mode (ν Te–O).

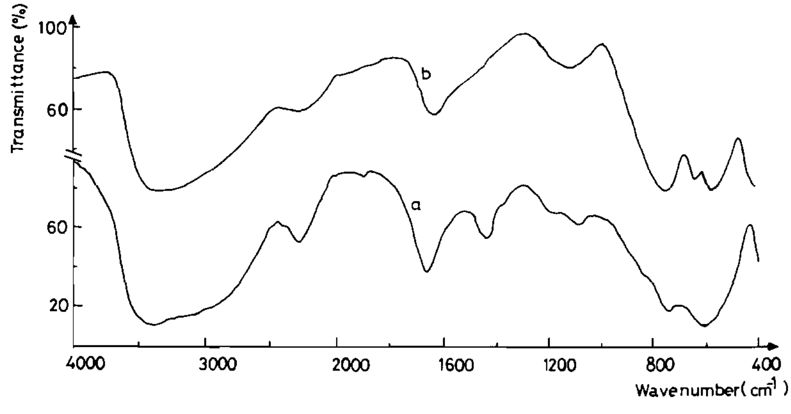

Figure 1. I.R. spectra of a) sodium ditellurato-aurate(III), b) sodium diperiodato-aurate(III).

The ditellurato-aurate(III) gave similar bands at 750 and 630 cm^{-1}, which can be similarly attributed to Te–O stretching mode.

Diperiodato-aurate(III)

By comparing the I.R. spectra of diperiodato-aurate(III) with those of orthoperiodic acid and its derivatives [7, 8], *meta* and *meso* periodates [7], evidence for the presence of hydrogen ions in the complex was got. The I.R. spectrum of the complex is given in Fig. 1b. Orthoperiodic acid [7] and iodic acid [9] absorb at 2900 cm^{-1} in I.R. This is unanimously attributed to the IOH stretching mode. These bands are slightly shifted toward lower wavenumbers for the salts of orthoperiodic acid [7]. For diperiodato-aurate(III), this band was observed as a shoulder band corresponding to the ν O–H of water of crystallisation (~7%) of the complex at 3400 cm^{-1}. The band at 2250 cm^{-1} can be attributed to the IOH (2δ IOH) bending mode, which is an overtone of the IOH group (δ IOH) at 1120 cm^{-1} (Fig. 1b). H. Siebert [7] observed these bands (2δ IOH) at 2200 cm^{-1} for H_5IO_6 and at 2260 cm^{-1} for $(NH_4)_2$ H_3IO_6, but these bands were missing for iodic acid [9]. The I.R. bands observed by D. Blink *et al.* [8] for $(NH_4)_2$-H_3IO_6 (2560 and 2300 cm^{-1}) and $Ag_2H_3IO_6$ (2560 and 2150 cm^{-1}) were attributed to ν O–H stretching mode of IOH group. The bands observed at 2300 and 2150 cm^{-1} by these authors are more likely to be due to an IOH bending mode which are overtones of the 1170 cm^{-1} band for $(NH_4)_2H_3IO_6$ and the 1160 cm^{-1} band for $Ag_2H_3IO_6$ [8]. Moreover, these authors attribute the peak at 1640 cm^{-1} to the δ IOH bending mode. We are of the same opinion as H. Siebert [7] that this band is due to the HOH bending mode, since such a band is absent in the orthoperiodic acid and its derivatives. This band was observed with the diperiodato-gold complex at 1630 cm^{-1} with a shoulder band at 1500 cm^{-1}. Analogous bands were found by H. Siebert [7] for $K_2HIO_5 \cdot 4H_2O$ at 1652 and 1602 cm^{-1}, which were attributed to δ HOH. Hence these results show that hydrated compounds had been used by R. Blink *et al.* [8] to study the I.R. spectra. There is a general agreement by workers [7–9] in this field that the band at 1100 cm^{-1} is due to the IOH bending mode (δ IOH). The spectrum of the gold complex also showed a band at 1120 cm^{-1} (Fig. 1b). The bands in the 800–500 cm^{-1} have been assigned as I–O stretching modes [7–9]. Three bands at 780, 600 and 540 cm^{-1} were observed for the gold complex and were assigned as I–O stretching modes. In addition to this, an I–O stretching mode was observed at 400 cm^{-1} and agrees with that found by Blink *et al.* [8]. It should be pointed out that the band observed at 400 cm^{-1} falls in the limit of detection of the method.

The infrared spectra of ditellurato- and diperiodato-aurate(III), compared with those of orthotelluric acid and its salts [6], meso and ortho periodates [7, 8] and iodic acid [9], allow the identification of the bending vibrations δ(Te OH) and δ(I OH) around 1100 cm^{-1}, with their overtones 2δ (Te OH) and 2δ (I OH)) near 2200 cm^{-1}. The O–H stretching vibrations of the Te OH and I OH groups are seen as shoulders of the OH stretching vibrations of the water of crystallisation.

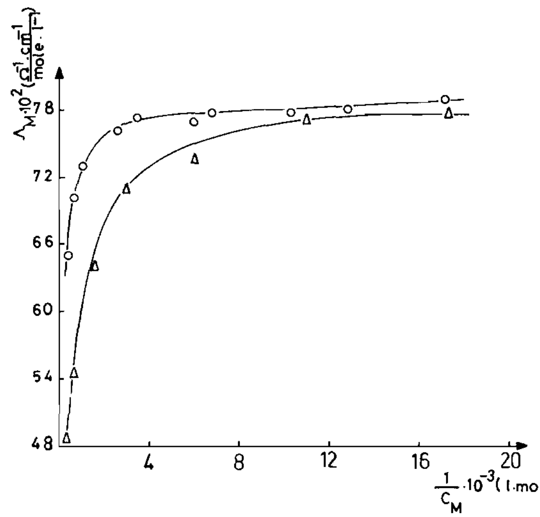

Figure 2. Conductimetric measurements of ○ sodium ditellurato-aurate(III), △ sodium diperiodato-aurate(III).

The fact that tellurates and periodates are found in the protonated forms contradicts the formulation of these complexes as $[Au(TeO_6)_2]^{9-}$ and $[Au(IO_6)_2]^{7-}$ [1–3]. Thus in order to clear doubts regarding the formulae of these complexes, conductimetric measurements were made to find the charge of the complex as well as the degree of protonation.

Conductimetric Measurements of Ditellurato- and Diperiodato-aurate(III)

Since this method seemed to give valid results for the anionic charge for the ditellurato- and diperiodato-cuprate(III) and argentate(III) complexes [4], the same procedure was adopted for the gold analogues.

The conductivity measurements were carried out with a Conductivity Meter LBR and a Metrohm conductivity cell. The cell constant was determined before each series of measurements. The concentration of the substances in aqueous solution under study was calculated using the stoichiometry of these complexes determined previously (*cf.* analytical study).

Λ_M *vs.* $1/C_M$ (C_M = molar concentration and Λ_M = molar conductivity) were plotted for ditellurato- and diperiodato-aurate(III) (Fig. 2) and the molar conductivity limit, Λ_∞, was determined from these plots. In both cases the limiting value was attained at $C_M \sim 10^{-4}$ *M* and Λ_∞ for ditellurato- and diperiodato-aurate(III) complexes were found to be 790 and 775 Ω^{-1} cm^2 mol^{-1} respectively. If the formulae of these complexes given previously [1, 2] are correct, then values of $\Lambda_\infty > 1350$ Ω^{-1} cm^2 mol^{-1} for ditellurato-aurate(III) and $\Lambda_\infty > 950$ Ω^{-1} cm^2 mol^{-1} for diperiodato-aurate(III) should be found. However, the results obtained by us were lower than these values suggesting that hydrogen ions are absent in aqueous solution. Moreover, the pH of the aqueous solution of these complexes remained unchanged. These results, together with the I.R. spectral and analytical studies, indicate that the anionic charges of these complexes are less than 9 and 7 for ditellurato- and diperiodato-aurate(III) respectively. For the calculation of the charge of the anionic species, a value of 100 Ω^{-1} cm^2 eq^{-1} for equivalent conductivity at 25 °C (λ_{25}) was chosen, this value being reasonable since equivalent conductivities of highly charged ions such as $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ are of this order of magnitude [10]. Thus an anionic charge of 5 seems to fit with experimental observation. Λ_∞, calculated using this assumption, was found to be 750 Ω^{-1} cm^2 mol^{-1}, which is in good agreement with the observed values of 790 and 775 Ω^{-1} cm^2 mol^{-1} for ditellurato- and diperiodato-complexes respectively. The calculated value for Λ_∞ is slightly lower than the observed ones because of the arbitrarily chosen value for λ. The values of λ at 25 °C (λ_{25}), for these complexes deduced from Λ_∞ were found to be respectively 108 and 105 Ω^{-1} cm^2 eq^{-1}.

Conclusion

The results of analytical, spectroscopic and conductimetric studies of ditellurato- and diperiodato-complexes are consistent with: a) a value of 1:5 for the Au:Na ratio; b) the presence of TeOH or IOH group in the complex, and c) an anionic charge of 5. Thus from the observed results we propose the following formulae for these complexes:

$[Au(H_2TeO_6)_2]^{5-}$: bis(dihydrogen tellurato)aurate(III).

$[Au(HIO_6)_2]^{5-}$: bis(hydrogen periodato)aurate(III).

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