Contribution to the Study of the Complexes Bis(dihydrogen tellurato)cuprate(III) and Argentate(III), Bis(hydrogen periodato)cuprate(III) and Argentate(III)

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The synthesis and characteristics of copper(III) and silver(III) complexes of tellurates and periodates are described. Chemical analysis, I.R. spectra and conductimetric measurements were used to determine the formulae of these anionic complexes, which were found to be: $[Cu(H_2TeO_6)_2]^{5-}$; $[Cu(HIO_6)_2]^{5-}$; $[Ag(H_2TeO_6)_2]^{5-}$ *and* $[Ag(HIO_6)_2]^{5-}$.

Introduction

Although the existence of copper(III) and silver(III) has been suspected since 1884, definite proof of their existence was obtained only by the works of Brauner and Kutzma [1]. Malaprade [3], who continued the work started by Vrtis [2] on copper(III), succeeded in isolating sodium cupriperiodate. Malatesta [4, 5] was the first to suggest that these compounds were coordination complexes and he proposed the following formulae:

$$Na_xH_y\, M^{III}(IO_6)_2 \cdot nH_2O$$

and

$$Na_{x'}H_{y'}\, M^{III}(TeO_6)_2 \cdot nH_2O$$
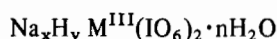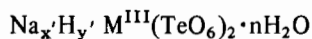
where $x + y = 7$
  $x' + y' = 9$
  M = Ag or Cu

This formulation is in accordance with that cited by L. Jensovsky *et al.* [6, 7] but has been questioned by Kirschenbaum *et al.* [8].

Ample evidence exists for the diamagnetism of Ag(III) and Cu(III) complexes [4, 5, 9–12]. Although there is no doubt that the bands obtained in the visible and the ultraviolet are charge transfer bands [13, 14], there is no consensus of opinion regarding the identification of maxima [13, 15].

The application of cuprate(III) or argentate(III) complexes in analytical chemistry has been studied by several authors [16–25]. Only a few of these authors have tried to elucidate the stoichiometric composition of these complexes and most of the

authors have taken for granted Malatesta's formulation. A point worth noting is that these authors obtain different degrees of protonation of these complexes whereas the anionic charge as given by Malatesta [4, 5] was undisputedly the same. Are these protons, if there are any, bonded by pure electrostatic attraction with the alkali metal ions or are they bonded to the metal like ligands as the work of Kirschenbaum *et al.* [8] seems to indicate?

The aim of this work has been to find out if the diperiodato and ditellurato cuprate(III) and argentate (III) are protonated and, if so, to find both the degree of protonation and the charge of the anionic component.

Synthesis of Complexes

Ditellurato-argentate(III)

This complex was synthesised by slightly modifying Jaiswal and Yadava's method [21]. All the reagents used were Merck *p.a.*: $AgNO_3$ (1.36 g), H_6TeO_6 (3.67 g), or K_2TeO_3 (4.06 g), $K_2S_2O_8$ (6.5 g) and KOH (9 g) were taken in a 500 ml round bottomed flask. 100 ml of demineralised water were added to this mixture. It is not important to follow this order of addition. The mixture was heated to boiling while stirring. After 15 minutes of boiling an orangish–yellow froth was obtained and the mixture was heated for another 15 minutes. The mixture was left to cool to room temperature and filtered through a Gooch crucible (the complex is instantaneously reduced on a filter paper). The solution was cooled in an ice bath to eliminate as much of potassium sulphate as possible and the solution filtered again while cold. The resulting orangish–red clear filtrate was left to attain room temperature. In order to isolate the complex, 40 ml of $NaNO_3$ solution (50%, in excess) were added to the solution and the mixture left to crystallise. Almost immediately crystals started appearing and crystallisation is complete (*ca.* 12 hr) when the supernatant liquid is colourless. The crystals were filtered and washed several times with

demineralised water until the complex itself starts dissolving, which is indicated by the orange—red drops being formed under the crucible. In this way one can be sure of eliminating sodium and potassium hydroxide since this complex is insoluble in concentrated hydroxide solutions.

Diperiodato-argentate(III)

The same procedure as that used for the synthesis of ditellurato-argentate(III) was used.

Reagents : $AgNO_3$ (1.36 g), $NaIO_4$ (3.42 g), $K_2S_2O_8$ (3 g), KOH (8 g). It is better to use sodium periodate rather than potassium periodate to avoid precipitation of potassium sulphate. The method of crystallisation was the same as described above and orangish—red crystals were obtained.

Ditellurato-cuprate(III)

The same procedure as described by Chandra and Yadava [19] was used to prepare this complex. For the sodium derivative the same method as described for the sodium salt of ditellurato-argentate(III) was used and found satisfactory. Reddish—brown flake-like crystals were obtained.

Diperiodato-cuprate(III)

The same experimental conditions as those given above were used. The reagents used were: $CuSO_4 \cdot 5H_2O$ (1.56 g), $NaIO_4$ (2.67 g), $K_2S_2O_8$ (1 g), KOH (8 g).

The crystallisation process was the same as described above and dark brown crystals were obtained.

Note: The diperiodato-argentate(III) was recrystallised by redissolving it in demineralised water at 80 °C and on filtering the hot solution, a whitish residue was left on the crucible. The same observation was made by G. L. Cohen *et al.* [15] and was attributed to the formation of a mixture of silver periodate and sodium periodate. We found a similar precipitate, but in smaller amounts, when ditellurato-argentate(III) was redissolved under the same conditions. The periodates were found to be darker than the tellurates and the cuprates darker than the argentates.

All the four sodium salts were found to be very soluble in water, but insoluble in concentrated sodium or potassium hydroxide solution, a result which is in perfect agreement with that of L. Jensovsky [6, 7].

It is rather strange that instead of starting from a sodium salt, the sodium salts of the complexes can be prepared by simple exchange reaction with the potassium salts. Attempts were made unsuccessfully to prepare the sodium ditellurato-argentate(III) from the following reagents: $AgNO_3$, H_6TeO_6, $(NH_4)_2S_2O_8$, NaOH, in the molar proportions

identical to those used with the potassium salt. L. J. Kirschenbaum *et al.* [8] have mentioned that G. L. Cohen had also tried without success a similar procedure in preparing $Ag(OH)_4^-$ by electrochemical oxidation of silver anode in concentrated caustic soda (12.0 M $\leqslant$ NaOH $\leqslant$19.3). Only L. J. Kirschenbaum *et al.* seem to have succeeded in this synthesis using 1.2 *M* NaOH. The reason for their success and the failure of others is not clear.

Absorption Spectra of the Diperiodato- and Ditellurato-cuprate(III) and Argentate(III) in UV—Visible Region

The positions of the absorption maxima for the complex diperiodato-argentate(III) cited in the literature are far from being in close agreement with one another [13, 15]. We have therefore tried to study this problem.

Solutions and Apparatus

After synthesising the different complexes (but before the exchange of potassium by sodium) the absorption spectra of these solutions and also those obtained from isolating and drying the crystals in dessiccator were measured. All the measurements were performed on a Beckman DB-G spectrophotometer connected to a Hi-Speed Recorder 1202 with 1 cm quartz cells.

Results and Discussion

The absorption spectrum of ditellurato-argentate(III) complex shows an absorption maximum at 355 $\pm$ 2 nm. This band was observed at 350 nm by L. Jensovsky *et al.* [13], at 351 nm by Kirschen-
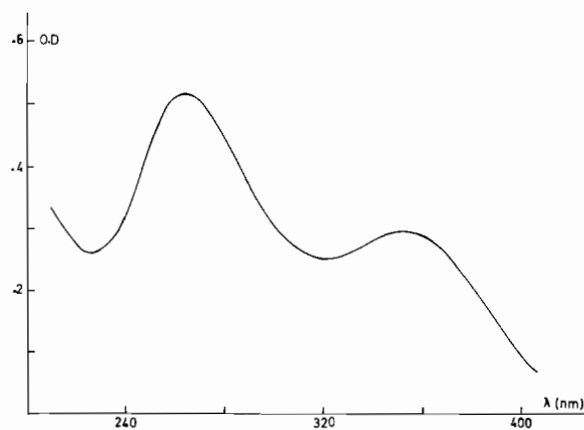

Figure 1. UV—visible spectrum of ditellurato-argentate(III) complex.

baum. We observed another band, after crystallisation, at 264 ± 2 nm (Fig. 1) which has not been mentioned by others.

The following table gives a summary of results of absorption spectrum of the diperiodato-argentate(III) complex together with those obtained by other workers:

	1st band max(nm)	2nd band max(nm)	3rd band max(nm)
L. Jensovsky	366	244	
G. L. Cohen	362	255	216
This work (Fig. 2)	363 ± 1	252.6 ± 0.4	

It can be seem from the above table that our results are in close agreement with those of G. L. Cohen [15]. The peak at 210–220 nm might be attributed to the periodate since those ions absorb in this region [26]. The spectrum of the crude complex shows an intense band at 216 nm which masks the band at 253 nm, and an inflexion is observed at 244 nm. However, a well defined peak at 252.6 ± 0.4 nm is observed with the recrystallised complex.

The results of the absorption spectra obtained for the diperiodato-cuprate(III) and ditellurato-cuprate(III) well agree with those observed by L. Jensovsky [13]. The first band is observed at 417 ± 5 nm and the second at 264 ± 2 nm for the diperiodato-cuprate(III), whereas L. Jensovsky obtains bands at 415 and 265 nm respectively. The ditellurato-cuprate(III) complex also shows two bands at 406 ± 3 nm and 274 ± 2 nm whereas L. Jensovsky obtains the same bands at 405 and 277 nm.

Study of I.R. Spectra of the Ditellurato- and Diperiodato-complexes of Copper(III) and Silver(III)

Not much attention has been paid to the protonation of the diperiodato- and ditellurato-cuprate(III) and argentate(III) complexes. This is obviously a difficult problem since the techniques such as NMR and I.R. have been relatively less applied in inorganic chemistry and, in addition, these complexes are soluble only in water. The NMR of these complexes in heavy water does not give any meaningful results, probably because of the hydration of the latter. Solid phase I.R. measurements give some useful results.

Preparation of Sample and Apparatus

The pellets for I.R. measurements were obtained by pressing the complex under study with potassium bromide in the ratio 1:100 and the spectra were taken using a Perkin–Elmer 357 spectrophotometer.

Results and Discussion

The water of crystallisation present in these complexes makes the analysis of results a little difficult.
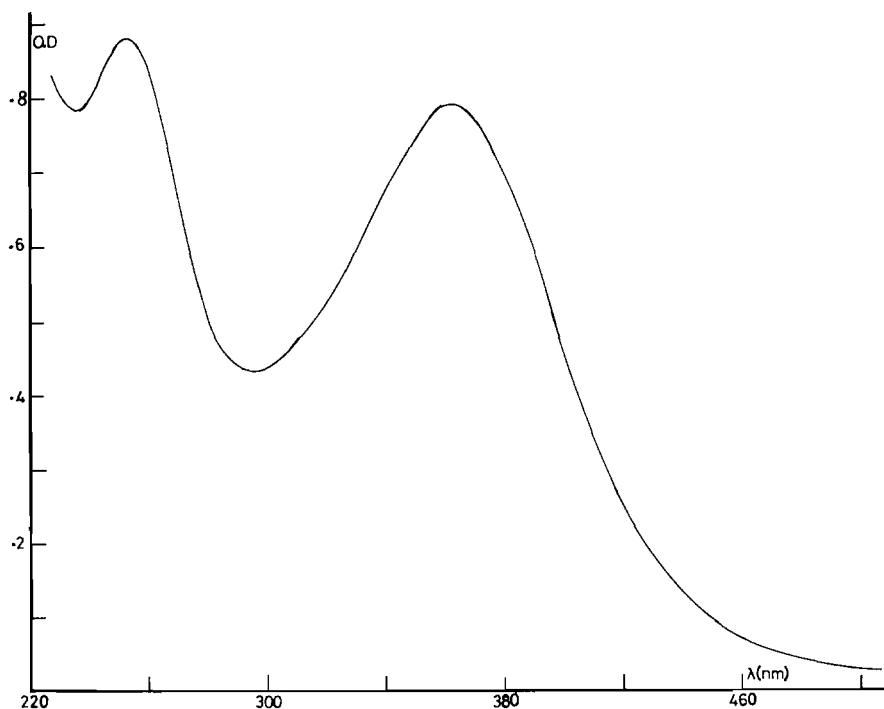

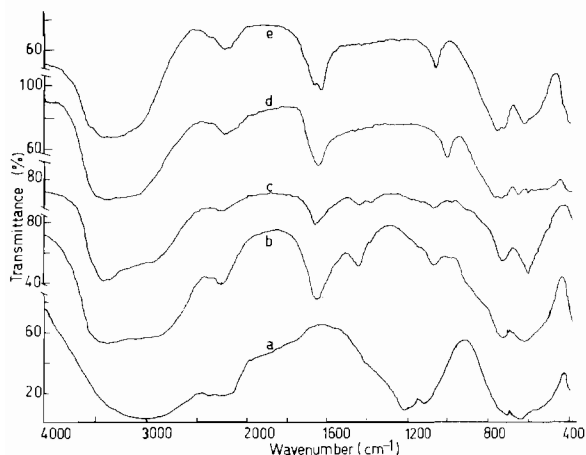Figure 2. UV–visible spectrum of diperiodato-argentate(III) complex.

Figure 3. I.R. spectra of a) telluric acid, b) sodium ditellurato-cuprate(III), c) sodium ditellurato-argentate(III), d) sodium diperiodato-cuprate(III), e) sodium diperiodato-argentate(III).

But by comparing the results of the works of W. H. Siebert [27] on telluric acid (H_6TeO_6), sodium tellurate (NaH_4TeO_6) and potassium tellurate ($K_2H_4TeO_6 \cdot 3H_2O$), we were able to draw some useful information.

The I.R. spectra of telluric acid (Fig. 3a), sodium ditellurato-cuprate(III) (Fig. 3b) and sodium ditellurato-argentate(III) (Fig. 3c) are shown. Siebert assigns the broad intense bands at 3100 cm^{-1} of H_6TeO_6 and $Na_2H_4TeO_6$, 3120 cm^{-1} of $K_2H_4TeO_6 \cdot 3H_2O$ to the valence-stretching vibration of the Te—OH bond (ν(Te—OH)). We observed similar bands around 3040 cm^{-1} in the case of telluric acid. In the case of ditellurato complexes of copper(III) and silver(III), this band (Fig. 3b, 3c) seems to overlap with that arising from the O—H vibration band of water [27, 28]. The band at 2250 cm^{-1} (Fig. 3b, 3c) spreading between 2400 and 2200 cm^{-1} (Fig. 3a) in the case of telluric acid is in agreement with that of Siebert and is perhaps due to the first harmonic Te—OH deformation band towards 1200 cm^{-1}. The ones at 1680 and 1490 cm^{-1} (Fig. 3b, 3c) and for $K_2H_4TeO_6 \cdot 3H_2O$ at 1630 and 1490 cm^{-1} [27] respectively, are attributed to the O—H deformation of the water molecule. In fact, these are absent from telluric acid, thus proving that telluric acid is really $Te(OH)_6$ as Siebert had pointed out. The band at 1060 cm^{-1} in the case of ditellurato-cuprate(III) complex (Fig. 3b) and appearing between 1060–1070 cm^{-1} for ditellurato-argentate(III) (Fig. 3c) corresponds to that at 1095 for $K_2H_4TeO_6 \cdot 3H_2O$ and would be Te—OH deformation modes having a harmonic band at 2250 cm^{-1}. The same author obtained bands between 800 and 600 cm^{-1} and we observe two bands quite clearly at 730 and 610 cm^{-1} with our complexes (Fig. 3b, 3c), which are hence

attributed to the Te—O valence-stretching vibration. The most important bands are observed at 740 and 610 cm^{-1} for $K_2H_4TeO_6 \cdot 3H_2O$.

Diperiodato-cuprate(III) and Argentate(III)

R. Blinc and D. Hadzi [29] in their study of infrared spectra of $Ag_2H_3IO_6$ and their deuterated analogues observed three bands due to the presence of protons in the region 3000 to 1500 cm^{-1}. We have also observed three bands of the copper(III) complex (Fig. 3d) at 1690 cm^{-1} with a shoulder at 1680 cm^{-1}, 2210 cm^{-1} and a broad band in the region 3600–2900 cm^{-1}, which certainly encompasses the O—H vibration mode of water. The same bands are clearly observed with the silver(III) complex at 1620 cm^{-1}, with a shoulder at 1660 cm^{-1}, at 2200 cm^{-1} and a broad band around 3300 cm^{-1} (Fig. 3e). The bands situated between 1500 and 1700 cm^{-1} are most probably due to O—H deformation [29]. In any case, these authors do not mention the presence of water molecules in their compounds; hence one would conclude that these bands are due to deformation of O—H bonded to iodine and not of O—H bonded to water, as stated by V. H. Siebert [27]. W. E. Dasent and T. C. Waddington [30], in their study of the vibrational spectra of iodic acid observe two bands due to O—H deformation at 1163 and 1101 cm^{-1}. We observe one band quite clearly at 1050 cm^{-1} (Fig. 3e) in the case of diperiodato-argentate(III) and a band at 1000 cm^{-1} (Fig. 3d) in the case of diperiodato-cuprate(III). These bands are attributed to O—H deformation considering the fact that the I—O or M—O (M = Cu or Ag) vibration frequencies are found to be below 850 cm^{-1} (28–30). Between 800 and 500 cm^{-1}, we observe a complex band for both diperiodato-cuprate(III) (Fig. 3d) and argentate(III) (Fig. 3e). Furthermore, R. Blinc and D. Hadzi [29] observe a band with several peaks between 590 and 700 cm^{-1} and they attribute this to the deformation mode of O—H. It must be pointed out that it is rather difficult to distinguish between the bands arising from I—O and O—H deformation modes in this region.

Conclusion

The similarity in the infra-red spectra of the ditellurato complexes of copper(III) and silver(III) indicates structural similarity in these complexes.

V. M. Siebert and W. E. Dasent et al. attribute the band around 1100 cm^{-1} to the deformation of —OH bound to tellurium [27] in H_6TeO_6, $Na_2H_4TeO_6$ and $Na_2H_4TeO_4 \cdot 3H_2O$ and to iodine in HIO_3 [30]. We observe (Fig. 3b, 3c, 3d, 3e) the same bands in this region and hence believe that the periodates and tellurates are protonated in these complexes. Different views are held concerning the assignment of the band found around 1600 cm^{-1}. According to V. H. Siebert [27] this band is due to O—H vibration

from water since this is absent in Te(OH)$_6$, whereas R. Blinc and D. Hadzi [29] attribute this band to the deformation mode of O–H bound to iodine in Ag$_3$H$_3$IO$_6$ and (NH$_4$)$_3$H$_3$IO$_6$. Our results conform with the assignment of V. H. Siebert since we do not observe a band with Te(OH)$_6$ and we think that perhaps the compounds studied by R. Blinc and D. Hadzi [29] were not completely anhydrous since we observe this in all our complexes which are hydrated (Fig. 3b, 3c, 3d and 3e). The band around 2200 cm^{-1} attributed to O–H bound to either tellurium [27] or iodine [30] was also observed in our complex (Fig. 3b, 3c, 3d and 3e).

The formulae of the silver(III) and copper(III) complexes previously proposed, [Cu(TeO$_6$)$_2$]$^{9-}$; [Ag(TeO$_6$)$_2$]$^{9-}$; [Cu(IO$_6$)$_2$]$^{7-}$ and [Ag(IO$_6$)$_2$]$^{7-}$ seem to be incorrect since none of these formulae have protons bound to the ligand.

Study of the Formulae of the Diperiodato- and Ditellurato-complexes of Copper(III) and Silver(III)

Determination of the Stoichiometric Composition

Preliminary analyses of the complexes were carried out using ESCA (electron spectroscopy for chemical analysis) in order to get an idea of the composition of these complexes. The instrument used for this purpose was a Varian IEE 15.

Results and Discussions

The results of this analysis are expressed as number of atoms per molecule of complex, except for water of crystallisation which is expressed as number of molecules.

Two values for silver and copper are given above because the analysis indicates that these elements are present in two oxidation states. The mixed oxidation states of the metals in the complexes are thought to be due to a reduction of Cu(III) and Ag(III) during the analysis. Moreover, satellites observed in ESCA make quantitative determination of these elements difficult. Hence the analysis of these metals has to be carried out by other analytical methods.

The ratio of iodine to oxygen bound to iodine was found to be 2:12, which is in agreement with that observed by other workers [4, 5, 9, 15]. It must be pointed out that the ESCA analysis enables us to distinguish between the oxygen bound to iodine or tellurium and oxygen of the water molecule. The ratio of I : O : Na = 2 : 12 : 5 (oxygen bound to iodine) is in accordance with that cited by G. L. Cohen *et al.* [15]. However, not much weight can be given to the number of water molecules present in these compounds, since ESCA analyses are carried out under vacuum ($\sim$10^{-7} mm Hg); at low pressure there is a strong probability of dehydration.

Analyses of these complexes were done by means of other analytical techniques in order to verify the results obtained by ESCA. The heavy metals (Ag, Cu) and alkali metals (Na, K) were analysed by atomic absorption and flame emission spectrophotometry, respectively. A Pye Unicam SP 1900 spectrophotometer was used for this purpose. Tellurate was analysed by differential pulse polarography using a PAR model 170; periodate was determined as described by G. L. Cohen *et al.* [15], water by thermogravimetric analysis using a Mettler analyser T.A. 1, and carbonate by classical microanalysis. These analyses gave the following results:

Diperiodato-argentate(III)

Ag	I	O	Na	K	H$_2$O
2.7 (0.3)	2	12	5	0	5

Diperiodato-cuprate(III)

Cu	I	O	Na	K	H$_2$O
1 (0.5)	2	12	4	1	3.8

Ditellurato-argentate(III)

Ag	Te	O	Na	K	H$_2$O
1.5 (1.2)	2	13	7	0	12.5

Ditellurato-cuprate(III)

Cu	Te	O	Na	K	H$_2$O
1 (0.8)	2	13.5	5	0	11.5

Diperiodato-argentate(III)

	Ag	IO$_6$	Na	K	H$_2$O	CO$_3$
Percentage :	12.12	46.77	12.88	0.02	23.77	0.00
Molar ratio :	1 :	1.87 :	4.99 :	0.005 :	11.75 :	0.00

Diperiodato-cuprate(III)

	Cu	IO$_6$	Na	K	H$_2$O	CO$_3$
Percentage :	7.53	48.72	13.06	1.09	31.25	0.00
Molar ratio :	1 :	1.84 :	4.79 :	0.24 :	14.65 :	0.00

Ditellurato-argentate(III)

	Ag	TeO$_6$	Na	K	H$_2$O	CO$_3$
Percentage :	11.19	47.85	13.20	0.02	22.73	2.35
Molar ratio :	1 :	2.06 :	5.53 :	0.005 :	12.17 :	0.38

Ditellurato-cuprate(III)

	Cu	TeO$_6$	Na	K	H$_2$O	CO$_3$
Percentage :	7.29	50.47	12.80	0.15	26.12	0.70
Molar ratio :	1 :	1.97 :	4.85 :	0.03 :	12.65 :	0.10

From these results it can be seen that the exchange of potassium by sodium is almost complete; the stoichiometric composition of these complexes is as follows: Cu(Ag) : $IO_6(TeO_6)$: Na = 1 : 2 : 5. These results, together with those deduced from infra-red measurements, lead one to suppose that the anionic charge on ditellurato-argentate(III) and ditellurato-cuprate(III) is less than 9 and the charge on diperiodato-cuprate(III) and diperiodato-argentate (III) less than 7. ESCA results showed 4–7 carbon atoms as carbonate ion, which is an artifact since I.R. spectra of these complexes do not show any peak in the finger point region of carbonate, *viz.* 1410–1450 and 840–880 cm^{-1}. Moreover, the chemical analysis also gave negative results for carbonate, except with ditellurato-argentate(III) which gave 2.35% for carbonate. The latter is attributed to the presence of sodium bicarbonate as impurity as the percentage of sodium in this complex was also found to be slightly high. Because of the low precision involved in the measurement of H_2O molecule by the thermogravimetric method, the sum of the percentage composition found was not exactly 100%. Nevertheless, this method was employed rather than the Karl–Fischer method because of the unsuitability of the latter in our case.

Determination of Anionic Charge

Electrophoresis, which is generally used for this type of study, could not be used here because the supporting material on which measurements are usually carried out is oxidised by these complexes. Hence conductimetric measurements were used for this study. The measurements were made at 25 °C with a LBR conductivity meter and a Metrohm conductivity cell.

The concentrations of these anionic complexes were carried out by dissolving the complexes in demineralised water (pH 7–8) and the heavy metals were analysed by atomic absorption spectrometry. Sodium and potassium were determined by flame photometry.

Results and Discussion

From the relation $\Lambda_M = f(1/C_M)$, where Λ_M is the molar conductivity and C_M the molar concentration, the molar conductivity at infinite dilution can be found. The molar conductivities experimentally observed were 610, 680, 786, 690 Ω^{-1} cm^2 mol^{-1} respectively for the complexes sodium diperiodato-argentate(III), sodium diperiodato-cuprate(III), sodium ditellurato-argentate(III) and sodium ditellurato-cuprate(III) (Fig. 4). These results show that protons are not liberated when the complex is dissolved since the liberation of two protons per molecule of complex would lead to a molar conductivity of 1300 Ω^{-1} cm^2 mol^{-1}. Further evidence against this assumption for the existence of protons in these complexes comes from the fact that these complexes can be prepared only in highly basic media and also that there is no decrease in pH when these complexes are dissolved in water. Furthermore, these complexes decompose even in slightly acidic medium.

Our results show that the formulations generally given, $[Ag(IO_6)_2]^{7-}$, $[Cu(IO_6)_2]^{7-}$, $[Ag(TeO_6)_2]^{9-}$ and $[Cu(TeO_6)_2]^{9-}$, are incorrect. If hydrogen atoms attached to periodate and tellurate are taken into account, then the possible anionic charges would be 5, 3 or 1 for diperiodato-complexes of copper(III) and silver(III) and 7, 5, 3 or 1 for the ditellurato-complexes of copper(III) and silver(III). The ratio of Ag:Na and Cu:Na would then be 1:5, 1:3 or 1:1 for the diperiodates and 1:7, 1:5, 1:3 or 1:1 for the ditellurates. We find, like L. Cohen and G. Atkinson [15], that this ratio is 1:5 in the case of diperiodato-
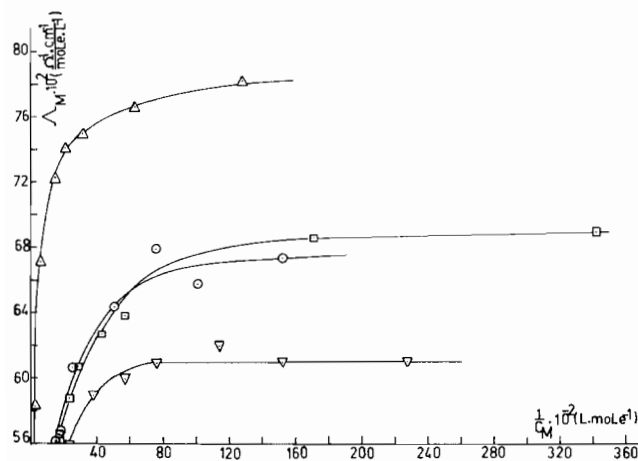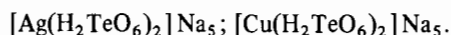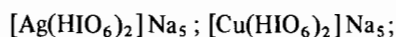

Figure 4. Conductimetric measurements of complexes: ▽ sodium diperiodato-argentate(III), ○ sodium diperiodato-cuprate(III), □ sodium ditellurato-cuprate(III), △ sodium ditellurato-argentate(III).
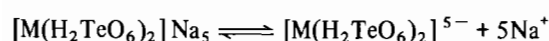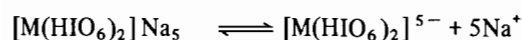
argentate(III). Other works in this field show that the ratio varies from one work to another (1:5 ± 2). In any case, the ratio 1:3 has been observed only in the case of $K_3H_4Ag(IO_6)_2 \cdot 3H_2O$ [6] and the 1:1 ratio has never been observed.

Our analysis leads us to suggest an anionic charge of 5 since the Ag:Na and Cu:Na ratio was found to be 1:5.

From the above results, the formulae of the complexes (without taking into account water of crystallisation) can be written as follows:

$[Ag(HIO_6)_2]Na_5$; $[Cu(HIO_6)_2]Na_5$;

$[Ag(H_2TeO_6)_2]Na_5$; $[Cu(H_2TeO_6)_2]Na_5$.

In solution this will dissociate into:

$[M(HIO_6)_2]Na_5 \rightleftharpoons [M(HIO_6)_2]^{5-} + 5Na^+$

$[M(H_2TeO_6)_2]Na_5 \rightleftharpoons [M(H_2TeO_6)_2]^{5-} + 5Na^+$
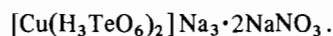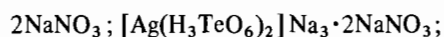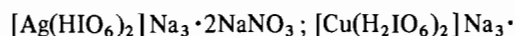
M = Ag or Cu

For comparison purpose, an approximate value of 100 Ω^{-1} cm^2 eq^{-1} was chosen for equivalent conductivity at infinite dilution for the studied complexes since one finds the same order of magnitude for the conductivities of highly charged species such as $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$. The values of 50 and 74 Ω^{-1} cm^2 eq^{-1} were taken for the conductivities of sodium and potassium ions respectively [32]. Using these values, the calculated value for the molar conductivity of these complexes is 750 Ω^{-1} cm^2 mol^{-1}, whereas experimentally observed values are 610, 680, 786 and 690 Ω^{-1} cm^2 mol^{-1} for sodium diperiodato-argentate(III), sodium diperiodato-cuprate(III), sodium ditellurato-argentate(III) and sodium ditellurato-cuprate(III), respectively. One can say at first glance that a value of 100 Ω^{-1} cm^2 eq^{-1} chosen arbitrarily well agrees with the experimental observations, although there is a large deviation for diperiodato-argentate(III).

The assumption for the charge on the anion of seven for the tellurate complexes of copper(III) and silver(III) can be refuted for, in order to satisfy electroneutrality law, there must be two more sodium ions, which will lead to a molar conductivity greater than 950 Ω^{-1} cm^2 mol^{-1}, and this is completely contradictory with the observed results.

The deviation observed can be attributed to either an error in Λ_∞ fixed arbitrarily at 100 Ω^{-1} cm^2 eq^{-1}, or to an error in the charge which instead of 5 is actually 3. If this were so, the complex will crystallise with two molecules of sodium nitrate (salt used for ion exchange) and would lead to the following formulation:
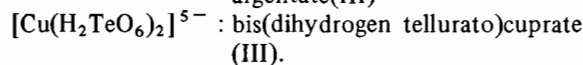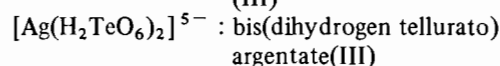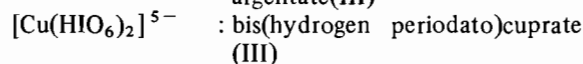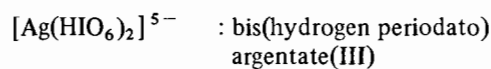
$[Ag(HIO_6)_2]Na_3 \cdot 2NaNO_3$; $[Cu(H_2IO_6)_2]Na_3 \cdot$

$2NaNO_3$; $[Ag(H_3TeO_6)_2]Na_3 \cdot 2NaNO_3$;

$[Cu(H_3TeO_6)_2]Na_3 \cdot 2NaNO_3$.

This calculation, using the above formulation, will give a value of Λ_∞ equal to 693 Ω^{-1} cm^2 mol^{-1}. It might be tempting to use this value to confirm a charge of 3 on the anionic complex and co-precipitation of $NaNO_3$ might even justify the ratio Ag:Na or Cu:Na = 1:5. However, the high solubility of sodium nitrate (92.1% at 25 °C) [33], and the reproducibility of the results for the ratio of Ag:Na and Cu:Na equal to 1:5, together with the agreement with the results of L. Cohen and G. Atkinson [15] who used NaOH for the exchange reaction and the absence of nitrate band in the I.R. spectral regions 1350–1380 and 815–840 cm^{-1} point against the above assumption. Hence only a charge of 5 conforms to the experimental results and the deviation can be attributed solely to the arbitrarily chosen value of Λ_∞ of 100 Ω^{-1} cm^2 eq^{-1}. It is apparent that the value would be slightly less than 100 Ω^{-1} cm^2 eq^{-1} for diperiodato-argentate(III), diperiodato-cuprate (III) and ditellurato-cuprate(III) complexes and slightly greater than 100 for ditellurato-argentate(III).

Conclusion

The infra-red, analytical and conductimetric measurements used for the study of copper(III) and silver(III) complexes suggest the presence of protons in these complexes which are bonded to periodate (I–OH) and tellurate (Te–OH) ligands. Also, these observations enable us to determine the charge on the anion which was found to be 5 instead of 7 for diperiodato-argentate(III) and cuprate(III), and 5 instead of 9 for ditellurato-argentate(III) and cuprate (III).

Moreover, in the light of the observed results, we propose the following formulae for the complexes:

$[Ag(HIO_6)_2]^{5-}$: bis(hydrogen periodato) argentate(III)

$[Cu(HIO_6)_2]^{5-}$: bis(hydrogen periodato)cuprate (III)

$[Ag(H_2TeO_6)_2]^{5-}$: bis(dihydrogen tellurato) argentate(III)

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

References

1 B. Brauner and B. Kutzma, *Ber.*, *40*, 3369 (1907).
2 M. Vrtis, *Rec. Trav. Chim.*, *44*, 424 (1925).
3 L. Malaprade, *Compt. Rend.*, *204*, 979 (1937).
4 L. Malatesta, *Gazz. Chim. Ital.*, *71*, 467 (1941).
5 L. Malatesta, *Gazz. Chim. Ital.*, *71*, 580 (1941).
6 L. Jensovsky, *Z. Anorg. Allg. Chemie*, *312*, 26 (1961).
7 L. Jensovsky and M. Skala, *Z. Anorg. Allg. Chemie*, *307*, 208 (1961).
8 L. J. Kirschenbaum, J. H. Ambrus and G. Atkinson, *Inorg. Chem.*, *12*, 2833 (1973).

9 L. Jensovsky and M. Ralek, *Z. Anorg. Chemie, 314,* 76 (1962).

10 R. S. Banerjee and S. Basu, *Inorg. Nucl. Chem., 27,* 353 (1965).

11 E. Barefield and M. T. Mocella, *Inorg. Chem., 12,* 2829 (1973).

12 J. A. McMillan, *Chem. Rev., 62,* 65 (1962).

13 L. Jensovsky, *Coll. Czech. Chem. Comm., 22,* 1996 (1967).

14 D. C. Olson and J. Vasilenskis, *Inorg. Chem., 10,* 463 (1971).

15 G. L. Cohen and G. Atkinson, *Inorg. Chem., 12,* 1741 (1964).

16 G. Beck, *Anal. Chim. Acta, 9,* 241 (1953).

17 K. G. Stone, "Determination of Organic Compounds", McGraw–Hill, New York (1956).

18 D. A. Keyworth and K. G. Stone, *Anal. Chem., 27,* 833 (1955).

19 S. Chandra and K. L. Yadava, *Talanta, 15,* 349 (1968).

20 S. Chandra and K. L. Yadava, *Microchem. J., 13,* 586 (1969).

21 P. K. Jaiswal and K. L. Yadava, *Talanta, 17,* 586 (1968).

22 P. K, Jaiswal, *Chim. Anal., 53,* 96, 254, 386, 457, 631 (1971).

23 P. K. Jaiswal, *Analusis, 1,* 503 (1971).

24 E. Casassas and J. P. Gonzalez, *Quim. Ind., 16,* 13 (1970).

25 W. G. Movius, *Inorg. Chem., 12,* 31 (1971).

26 C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, *J. Am. Chem. Soc., 71,* 3031 (1949).

27 V. H. Siebert, *Z. Anorg. Allg. Chemie, 301,* 161 (1959).

28 H. A. Szymanski, "Progress in Infra-Red Spectroscopy", Vol. 1, Plenum, N. Y. (1962).

29 R. Blinc and D. Hadzi, *Mol. Phys., 1,* 391 (1958).

30 W. E. Dasent and T. C. Waddington, *J. Chem. Soc.,* 2429 (1960).

31 B. M. Gatehouse, S. E. Livingston and R. S. Nyholm, *J. Chem. Soc.,* 3137 (1958).

32 R. A. Robinson and R. H. Stokes, "Electrolytes Solutions", 2nd Edition, London Butter Scientific Publications (1959).

33 "Handbook of Chemistry and Physics", C. R. C., 54th Edition, B-139 (1973–1974).