

Thermal, Electrical & Spectral Properties of Bis(8-quinolinolato)-gold(III)-tetrachloroaurate(III)

KARUNAMAY BANERJEE* & SWAPAN K BOSE†

Department of Pure Chemistry, Calcutta University,
Calcutta 700 009

and

PRABIR K GUPTA‡

Department of Plastics & Rubber Technology, Calcutta University,
Calcutta 700 009

Received 1 April 1985; revised and accepted 27 May 1985

Bis(8-quinolinolato)gold(III)-tetrachloroaurate(III) exhibits two forms, green and amber in colour. The green variety transforms into the amber variety on heating. The two varieties, which correspond to the same formation $[\text{Au}^{\text{III}}\text{Q}_2][\text{Au}^{\text{III}}\text{Cl}_4]$, exhibit similar IR spectra but dissimilar electrical conductances in solution as well as in the solid state. The amber form shows semiconducting behaviour in the solid state and the absence of a low energy optical transition around 18000 cm^{-1} . The green form shows unchanged resistance on increasing temperature and an optical band around 18000 cm^{-1} . The presence of $\sim 18000\text{ cm}^{-1}$ band in the reflectance spectrum of the amber variety is due to anion ($5d_z$) to cation ($6p_z$) charge-transfer transition.

Gold(III) is reported¹ to form two varieties of complexes (green and amber) with 8-quinolinol (HQ) having the same formula, $[\text{Au}^{\text{III}}\text{Q}_2][\text{Au}^{\text{III}}\text{Cl}_4]$. The present note reports the results of thermal and IR spectral studies in solid state, and the electrical conductance and electronic spectral studies in solution and solid state for both the varieties of the gold(III) complex in order to resolve their hitherto unaccounted characteristic features.

All the reagents were of AR or CP grade. The green and amber varieties of bis(8-quinolinolato)gold(III)-tetrachloroaurate(III) were prepared by the methods of Inazu¹. The thermal analysis of the green form (150-200 mesh) was carried out using a Shimadzu DTA instrument model DT 30 in a constant flow of dry air at a heating rate 10° min^{-1} . Enthalpy change (ΔH) was estimated from the DTA peak area using zinc metal as the calibrant.

The reflectance and solution spectra of the samples were recorded on a Cary D17 spectrophotometer and the far IR spectra (polythene disc) were recorded on a Polytech FIR 30 spectrophotometer.

The molar conductivities were recorded on an Elico CM 82T instrument. The electrical resistance of the

powdered sample was measured (303-343 K) by a platinum wire-fitted glass capillary cell (1 mm $\times$ 10 mm) using a B.P.L. (India) megohmmeter set-up. The thermal activation energy (ΔE) was calculated from the resistance-temperature plot.

The DTA curve of the green variety of $[\text{Au}^{\text{III}}\text{Q}_2][\text{Au}^{\text{III}}\text{Cl}_4]$ complex reveals an exothermic peak [321.7-331.0 K (endo), peak temp. 325.7 K; ΔH , 0.54 kJ mol^{-1}] without any inflection in the TG curve. The product obtained by heating the green variety at 331 K exhibits IR and reflectance spectra (Table 1, Fig. 1), and thermal and elemental analyses similar to those of the amber variety [Green variety at 331 K: 388.0-418.0 (exo), peak temp. 399 K; ΔH , 176.80; Found: N, 3.42; Cl, 17.19; Au, 47.78. Amber variety: 388.0-418.0 K (exo), ΔH , $176.80\text{ kJ mol}^{-1}$; Found: N, 3.42; Cl, 17.18; Au, 47.78. $\text{Au}_2\text{C}_{18}\text{Cl}_4\text{H}_{12}\text{N}_2\text{O}_2$ requires N, 3.40; Cl, 17.22; Au, 47.80 %]. The decomposition of the sample starts above 388 K as indicated by the exotherm and loss in mass. A similar observation was reported² in the two varieties of $\text{Cu}^{\text{II}}\text{Q}_2$ complex.

The steady decreasing trend of the electrical resistance with increase in temperature for the amber variety of the gold (III) complex suggests its semiconducting behaviour; it has thermal activation energy of 0.56 eV ($\sim 4500\text{ cm}^{-1}$). On the other hand, the green variety shows almost unchanged resistance up to 331 K, and shows a decreasing trend only after 331 K. This observation together with the thermal analysis indicates the transformation of the green form to the amber form at 331 K.

Table 1—Electronic Spectral Data

$[\text{Au}^{\text{III}}\text{Q}_2]\text{-}[\text{Au}^{\text{III}}\text{Cl}_4]$	Solution spectra $\bar{\nu} \times 10^{-3}, \text{ cm}^{-1} (\epsilon)$	Reflectance spectra $\bar{\nu} \times 10^{-3}, \text{ cm}^{-1} (\text{nm})$
Green*	DMSO 17.7 (600), 26.4 (4500), 31.5 (6400) DMSO (5%) + Ethanol 18.2 (1200), 26.7 (3800), ~ 32 (9200), 39.4 (20600), 41.6 (52100)	~ 23.53 (425), ~ 16.67 (600)
Amber*	DMSO 26 (2450), 31.1 (12000) DMSO (5%) + Ethanol 25.2 (1800), ~ 31 (5500), 38.5 (16000), 41.3 (53800)	~ 23.53 (425) ~ 16.67 (600)
Amber**		~ 23.26 (430), ~ 16.67 (600)

*Prepared¹; **Obtained on heating the green form at 331 K.

†Present address: Eye Research Institute, 20 Staniford Street, Boston, Ma 02114, USA.

‡Executive Editor, Indian Chemical Society, Calcutta 700 009.

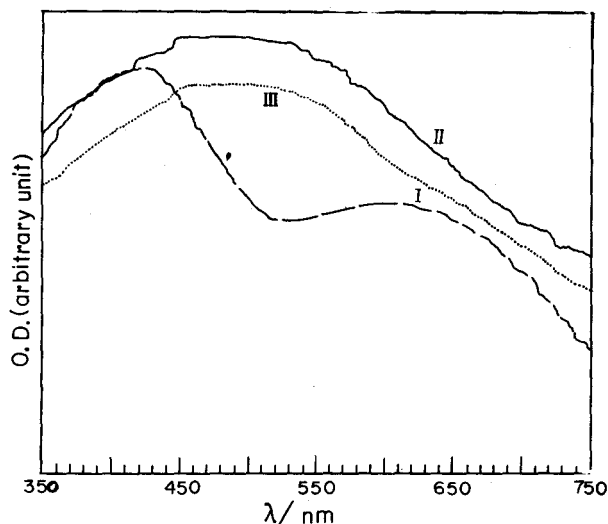


Fig. 1—Reflectance spectra of $[\text{Au}^{\text{III}}\text{Q}_2][\text{Au}^{\text{III}}\text{Cl}_4]$: (I) Green; (II) amber; (III) green after heating at 331 K

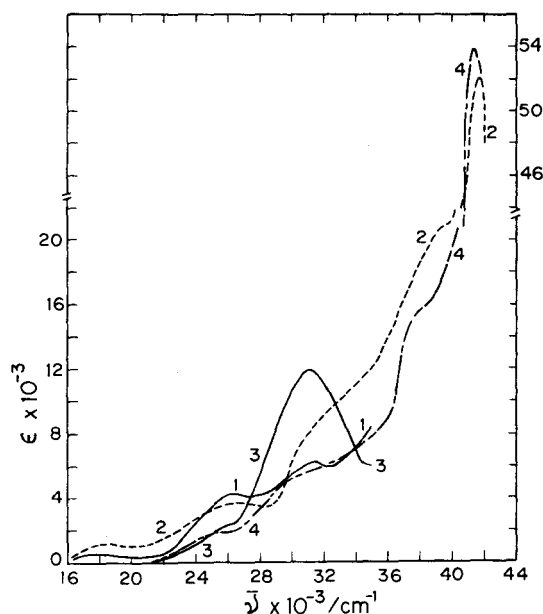


Fig. 2—Absorption spectra of $[\text{Au}^{\text{III}}\text{Q}_2][\text{Au}^{\text{III}}\text{Cl}_4]$: (1) Green variety in DMSO; (2) green variety in DMSO (5%) + ethanol; (3) amber variety in DMSO; (4) amber variety in DMSO (5%) + ethanol

The electronic spectra of both the varieties of $\text{Au}(\text{III})$ complex exhibit intense bands in DMSO-ethanol at ~ 41000 and $\sim 31000 \text{ cm}^{-1}$, and in DMSO at $\sim 31000 \text{ cm}^{-1}$ (Table 1, Fig. 2). The appearance of these bands may be due to $\text{Cl} \rightarrow \text{Au}$ charge-transfer transitions^{3,4}. A band at $\sim 26000 \text{ cm}^{-1}$ for both the varieties is assigned to red shifted 1L_a transition with considerable $d \rightarrow \pi^*$ charge-transfer component. The 39000 cm^{-1} band in DMSO-ethanol for both the varieties is due to the unaffected 1B_b transition, similar to those observed⁵⁻⁷ for $\text{Cu}^{\text{II}}\text{Q}_2$ and $\text{Ni}^{\text{II}}\text{Q}_2$ complexes. It is known⁶ that unaffected 1L_b band in quinolinolates appear at 31000 cm^{-1} . In the present case the appearance of a

broad band at $\sim 31000 \text{ cm}^{-1}$ for both the varieties may be due to 1L_b transition and $\text{Cl} \rightarrow \text{Au}$ charge-transfer in the cationic and anionic parts of the complex, respectively.

The reflectance spectra (Fig. 1) exhibit two well-resolved bands at $\sim 425 \text{ nm}$ ($\sim 23530 \text{ cm}^{-1}$) and $\sim 600 \text{ nm}$ ($\sim 16670 \text{ cm}^{-1}$) for the green variety and a broad band at $\sim 425\text{--}600 \text{ nm}$ ($23530\text{--}16670 \text{ cm}^{-1}$) for the amber variety of the gold (III) complex. The most distinguishing observation in the solution spectra (Fig. 2) is the presence of a broad band at 18000 cm^{-1} ($\epsilon \sim 500$) in the case of green variety and its total absence in the amber one. This high molar absorptance in the solution spectra of the green variety overrules $d\text{--}d$ transition and precludes metal $\rightarrow$ ligand charge-transfer transition as it appears at a much lower energy in comparison to that in $\text{Ni}^{\text{II}}\text{Q}_2$ complex⁶. Therefore, the presence of the low energy band ($\sim 18000 \text{ cm}^{-1}$) in both the solid and solution spectra of the green variety suggests intramolecular $5d_{z^2} \rightarrow 6p_z$ transition with interatomic $5d_{z^2}(\text{atom a}) \rightarrow 6p_z(\text{atom b})$ charge-transfer excitation⁸. The thermal activation energy calculated from resistance-temperature graph for amber variety is found to be 0.56 eV (4500 cm^{-1}). It is possible to get an estimate close to this value, from optical transition in the reflectance spectra (Fig. 1) of amber variety taken to be centred around 550 nm (18180 cm^{-1}), by the relation $E_{\text{thermal}} \approx \frac{1}{4} E_{\text{optical}}$ as in the case of intervalence transfer band⁹. Therefore, presence of $\sim 18000 \text{ cm}^{-1}$ band in the solid state spectra and the semiconducting nature of the amber variety suggest^{8,9} anion ($5d_{z^2}$) to cation ($6p_z$) charge-transfer in the solid state. In the solution state this band ($\sim 18000 \text{ cm}^{-1}$) extinguishes due to enhanced ionic character of amber variety.

The intensity of 1L_a band ($\sim 26000 \text{ cm}^{-1}$) decreases on adding ethanol to the DMSO solution of each variety of $\text{Au}(\text{III})$ complex. Ethanol (a hydrogen bonding component) binds the lone pair of oxygen atom of the 8-quinolinolates and makes it unavailable to the heterocyclic ring and thus 1L_a transition (which is due to charge-transfer from O^- to the heterocyclic π^* system) is hindered. Analogous hydrogen bonding is known¹⁰ between solvent chloroform and oxygen atom of $\text{Cu}^{\text{II}}(\text{SE})$, where H_2SE is $\text{N,N}'$ -bis(salicylidene)diaminoethane. Simultaneous increase in the intensity of $\sim 18000 \text{ cm}^{-1}$ band (i.e., $5d_{z^2} \rightarrow 6p_z$) of the green form of $\text{Au}(\text{III})$ complex is probably due to the compensation effect of hydrogen bonding.

The molar conductance values for the green variety in DMSO and DMSO-ethanol (9:1, v/v) media are 38.6 and 61.06 S cm^2 , respectively which are lower than the corresponding values for the amber one (115.3 and 88.24 S cm^2). Relatively higher values exhibited by the amber form in both the solvents suggest its enhanced ionic nature (1:1 electrolyte)¹¹, having greater

ionization in higher dielectric medium. The reverse is true for the green variety.

The main far IR bands, $\nu\text{Au}-\text{O}$, $\nu\text{Au}-\text{N}$, $\nu\text{Au}-\text{Cl}$, $\text{Au}-\text{Cl}$ in-plane bending and $\text{Au}-\text{Cl}$ out-of-plane bending vibrations for green and amber forms are observed at respectively, 435 and 428; 380 and 370; 358, 345, 313 and 352, 342, 310; 175 and 174; 142, 140 and 145, 138 cm^{-1} . The far IR spectra indicate that except for metal-ligand vibrations all other frequencies for both the varieties of the Au(III) complex are similar to those reported for $\text{Cu}^{\text{II}}\text{Q}_2$ complex¹²⁻¹⁴. This suggests structural similarity in the $[\text{Au}^{\text{III}}\text{Q}_2]^+$ part for both the varieties of the gold complex.

The IR spectra indicate shifting of 1090 cm^{-1} (phenolic $\nu\text{C}-\text{O}$) band of the free ligand¹⁵ to 1105 and 1098 cm^{-1} for the green and amber forms, respectively indicating change from hydrogen bonded structure to more covalent metal bonded one. The $\nu\text{C}=\text{N}$ for 8-quinolinol at 1580 cm^{-1} is shifted to higher frequency at 1605 cm^{-1} for the amber form and to lower frequency at 1575 cm^{-1} for the green form of the Au(III) complex indicating comparatively less double bond character of the $\text{C}=\text{N}$ in the latter¹⁶⁻¹⁸.

In the case of the green variety, the charge-transfer from O^- to the heterocyclic ring (1L_a) occurs at a higher energy in comparison to that in the amber one. Similar to the dual forms of the $\text{Cu}^{\text{II}}\text{Q}_2$ complex^{2,19,20}, there may exist a weak binding between the gold atom of $[\text{Au}^{\text{III}}\text{Q}_2]^+$ with the oxygen lone pair of the other $[\text{Au}^{\text{III}}\text{Q}_2]^+$, resulting in depletion of the electron density of the π system of quinoline. This accounts for higher energy value of 1L_a band and lower double bond character of $\text{C}=\text{N}$ (as shown by the IR spectra) of the

green variety of the complex. Such weak binding persists even in the solution state of the green variety resulting in its lower molar conductance value and its exhibiting of similar solid and solution state spectra. Probably electron delocalisation between metal centres existing in the solid state of the amber variety is responsible for its semi-conducting behaviour and the colour difference. X-ray data could perhaps elaborately resolve the nature of the two varieties of the Au(III) complex.

The authors thank Mr Gopal C Maity and Mr Sushil K Dey, Department of Chemistry, University of Calcutta for assistance.

References

- 1 Inazu T, *Bull chem Soc Japan*, **39** (1966) 1065.
- 2 Fanning J C & Jonassen H B, *J inorg nucl Chem*, **25** (1963) 29.
- 3 Gangopadhyay A K & Chakrabartty A, *J chem Phys*, **35** (1961) 2207.
- 4 Roy Mason II W & Gray H B, *Inorg Chem*, **7** (1968) 55.
- 5 Perkampus H H & Kortum K, *Z analyt Chem*, **190** (1962) 111.
- 6 Morpurgo L & Williams R J P, *J chem Soc(A)*, (1966) 73.
- 7 Ohasi Y, Hanazaki I & Nagakura S, *Inorg Chem*, **9** (1970) 2551.
- 8 Thomas T W & Underhill A E, *Chem Soc Rev*, **1**(1) (1972) 99.
- 9 Allen G C & Hush N S, *Progr inorg Chem*, **8** (1967) 357.
- 10 Baker E N, Hall D & Waters T N, *J chem Soc(A)*, (1970) 406.
- 11 Geary W J, *Coord Chem Rev*, **7** (1971) 112.
- 12 Ohkaku N & Nakamoto K, *Inorg Chem*, **10** (1971) 798.
- 13 Sabatini A, Sacconi L & Schetting V, *Inorg Chem*, **3** (1964) 1775.
- 14 Miller J R, *J chem Soc*, (1965) 713.
- 15 Tacket J E & Sawyer D T, *Inorg Chem*, **3** (1964) 692.
- 16 Stouffer R C & Busch D H, *J Am chem Soc*, **82** (1960) 3491.
- 17 Busch D H & Bailar J C, *J Am chem Soc*, **78** (1956) 1137.
- 18 Kovacic J E, *Spectrochim Acta*, **23A** (1967) 183.
- 19 Palenik G J, *Acta Crystallogr*, **17** (1964) 687.
- 20 Roy R C & Morris R H, *Acta Crystallogr*, **22** (1967) 476.