Spectrochemical Study of Microscopic Crystals. XV[1]. *Structure and Light Absorption of Bis-(dimethylglyoximato) gold(III) Dichloro-aurate(I)*[2]

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In the former publications[3] the present authors reported on those compounds which display enormously deep colors owing to possible metal-to-metal interaction. A recent study indicated that bis-(dimethylglyoximato)-gold(III) dichloro-aurate(I), $[Au(dgH)_2][AuCl_2]$[4], would be a compound of a similar sort. Rundle[5] examined with X-ray the crystal structure of the compound, showing that in the crystal of the compound the linear dichloro-aurate(I), $[AuCl_2]^-$, and planar bis-(dimethylgyloximato)-gold(III) ions, $[Au(dgH)_2]^+$, are arranged parallel to each other, with the gold(I) and the gold(III) ions disposed at an equal distance along the *c*-axis of the crystal. Sinec the distance between the gold(I) and the gold(III) ions was found to be comparatively short, he assumed the existence of the direct interaction between the gold(I) and the gold(III) ions. As our former reports revealed that those compounds involving direct interaction between metallic ions showed an extraordinary type of dichroism, it was thought that it would be significant to examine dichroism of bis-(dimethylglyoximato)-gold(III) dichloro-aurate(I) with reference to the relationships on the dichroism which were formerly derived.

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[1] Part XIV of this series, S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 647 (1957).

[2] R. Tsuchida and S. Yamada, Presented before the Annual Meeting of Japan Chemical Society, Tokyo, April 6th, 1957.

[3] S. Yamada and R. Tsuchida, This Bulletin, **27**, 156 (1954); *J. Am. Chem. Soc.*, **73**, 1579 (1951); ibid., **75**, 6351 (1953), etc.

[4] The notation, dgH_2, represents a molecule of dimethylglyoxime.

In this work we have quantitatively determined the dichroism of the above-mentioned compound in the visible and the ultra-violet. The result has been found to disagree with the hypothesis of the existence of the metal-to-metal interaction in the present compound.

Experimental

Material.—The compound, $[Au(dgH)_2][AuCl_2]$ was prepared in brown needles according to the method reported by Rundle[5]. Crystals having an identical external form were always obtained in all of our experiments. A marked dichroism was observed under the microscope. The crystal is yellow with the electric vector along the *c*-axis and brownish orange with the electric vector normal to the *c*-axis. The dichroism measurement was carried out with polarized light having its electric vector along and normal to the *c*-axis. The *c*- and *a*-absorption represent the absorption with the electric vector along and normal to the *c*-axis, respectively.

Measurement.—Quantitative dichroism measurement was done by Tsuchida-Kobayashi's microscopic method using polarized light[6]. The symbols used here are the same as those in our former papers of this series.

Results and Discussion

The result of the dichroism measurement is shown in Fig. 1 and Table I. According to the crystal structure analysis of $[Au(dgH)_2][AuCl_2]$ reported by Rundle, the planar cations of $[Au(dgH)_2]^+$ and linear anions of $[AuCl_2]^-$ are arranged alternately in the crystal of the present compound such that the planes and the lines of the complex ions are parallel to each other and perpendicular to the *c*-axis, that is, the needle axis. The *c*-absorption is seen to correspond with the ⊥-absorption, the absorption with the electric vector normal to the direction in which lie the linkages of the ligands with the metallic ion. The *a*-absorption is found to represent the main features of the ∥-absorption of the complex ion; that is, the absorption with the electric vector along the linkage.

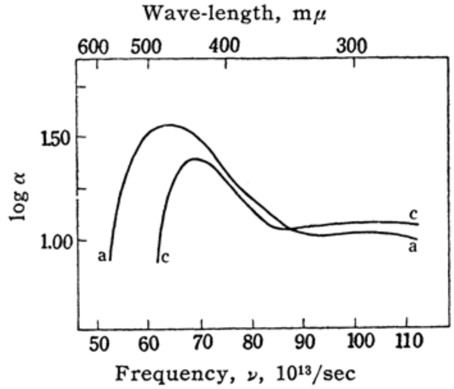

Fig. 1. Absorption spectra of $[Au(dgH)_2]$ $[AuCl_2]$ in the crystalline state.

The present measurement of dichroism shows that *for the absorption band at the longer wave-length, the ∥-absorption is about four and a half times as intense as the ⊥-absorption.*

From the short Au(I)-Au(III) distance of 3.26 Å, Rundle[5] suggested the existence of weak linkage between the Au(I) and Au(III) ions in the present compound. The weak metal-to-metal linkage as proposed for the present compound would be somewhat similar to the metal-to-metal linkage for Magnus's green salt, bis-(dimethylglyoximato)-nickel(II), and so forth. Our former researches[3] indicate that for the absorption band at the longer wave-length of those compounds involving the metal-to-metal interaction, absorption is stronger in the direction normal to the complex plane; i. e. in the direction in which the metal-to-metal linkage is expected to exist than along the plane of the complex. This is not the case with the present compound. Thus the present dichroism measurement seems to indicate that *the metal-to-metal interaction may not exist between the Au(I) and the Au(III) ions in the present compound.*

TABLE I

ABSORPTION MAXIMA OF $[Au(dgH)_2][AuCl_2]$

	ν, 10^{13}/sec.	log α	half width, 10^{13}/sec.
a-abs.	64	1.55	18
c-abs.	69	1.37	6.5

Assuming the absence of the metal-to-metal interaction between the Au(I) and the Au(III) ions, the absorption band at about 60–70×10^{13}/sec. may be due to the planar $[Au(dgH)_2]^+$ ions under slight perturbation from the surrounding ions, since the $[AuCl_2]^-$ ion is not expected to show absorption in this wave-length region. For planar metallic complexes involving no metal-to-metal interaction, previous studies[7] show that with the absorption band at the longer wave-length, electric vector is more strongly absorbed along the plane of the complex than along the direction normal to the complex plane.

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[5] R. E. Rundle, *J. Am. Chem. Soc.*, **76**, 3101 (1954).

[6] R. Tsuchida and M. Kobayashi, "The Colour and the Structure of Metallic Compounds", Zoshindo, Osaka, 1944, p. 180. See also the previous papers of this series.

[7] S. Yamada and R. Tsuchida, This Bulletin, **26**, 489 (1953); ibid., **29**, 289 (1956); ibid., **29**, 694 (1956); *Ann. Rep. Scient. Works, Fac. Sci. Osaka Univ.*, **4**, 79 (1956), etc.

A similar relationship may reasonably be expected for the dichroism of the planar $[Au(dgH)_2]^+$ ion. The relationship obtained with $[Au(dgH)_2][AuCl_2]$ is seen to agree with that for typical planar complexes without the metal-to-metal interaction. This fact is also compatible with the conclusion that the metal-to-metal interaction is absent in the present compound.

It is to be noted that the metal-to-metal interaction is absent in the crystal of $[Au(dgH)_2][AuCl_2]$, where the Au(I)-Au(III) distance is comparatively short and almost equal to the Ni-Ni distance in the crystal of $Ni(dgH)_2$, in which the metal-to-metal interaction was concluded to exist.

This difference between $[Au(dgH)_2][AuCl_2]$ and $Ni(dgH)_2$ will be discussed in the following part of the present paper. The ionic radius of Ni(II) in the molecule of $Ni(dgH)_2$ is expected to be larger than that of Au(III) in the ion of $[Au(dgH)_2]^+$, judging from difference in the electronic charge between them. This might be one of the reasons for the absence of the metal-to-metal interaction.

In addition to this, however, there may be another reason for this phenomenon, which we are inclined to regard as more important. The central nickel ion in the $[Ni(dgH)_2]$ molecule is assumed to have non-bonding *d*-electrons spreading in the regions above and below the metallic ion in the direction normal to the plane of the complex. These non-bonding *d*-electrons may be available for some additional bonding, since a very great amount of energy may not be required to promote these electrons for the additional bonding. It was assumed in the former papers[3,8] that the nickel ions lying at an equal distance along the *c*-axis form octahedral sp^3d^2 hybridization orbitals, overlapping of the orbitals being responsible for the metal-to-metal interaction. For the overlapping of the orbitals resulting in the metal-to-metal linkage may be used the non-bonding 3*d*-electrons which originally spread in the direction perpendicular to the plane. This seems to be consistent with the idea proposed by Rundle and Sturdivant[9], who pointed out that the existence of a low-lying orbital was necessary for the metal-to-metal linkage. The existence of electrons which can be promoted for the linkage with a comparatively small amount of energy may also be important.

As for $[Au(dgH)_2][AuCl_2]$, the $[Au(dgH)_2]^+$ ion involves similar situation to that of $[Ni(dgH)_2]$, the above condition for the metal-to-metal linkage being satisfied. On the contrary, the Au(I) ion in the $[AuCl_2]^-$ ion forms linear *sp* hydridization orbitals in the outside of the $5d^{10}$ closed shell. For the metal-to-metal linkage, the Au(I) must form square hybridization orbitals and at the same time electrons in the $5d^{10}$ closed shell must be available. We prefer to suppose that the considerably great stability of the $5d^{10}$ closed shell might make the above conditions difficult to be fulfilled. Thus the conclusion that the Au(I)-Au(III) interaction is absent in the present compound may be understood on the basis of these considerations.

In advancing the hypothetical metal-to-metal linkage in the present compound, Rundle[5] assumed $5d6s6p^2$ hybridization orbitals of the Au(I) ion which would result in overlapping with some of the hybridization orbitals of the Au(III) ion. A comparatively great amount of energy may be required for the $5d6s6p^2$ hybridization because of the possibly great stability of the $5d^{10}$ closed shell. In our view on the basis of the present observation, the hybridization of $5d6s6p^2$ can hardly be assumed to occur at such a distance as observed for the crystal of the present compound.

Summary

Dichroism of $[Au(dgH)_2][AuCl_2]$ has been determined in the visible and the ultraviolet region by the microscopic method. For the absorption band at about $60–70\times10^{13}$/sec., absorption has been found to be about four and a half times as strong along the complex plane as along the direction normal to the plane.

From discussion on the result of the dichroism measurement, it has been concluded that the metal-to-metal interaction does not exist between the Au(I) and Au(III) ions in this crystal.

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[8] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[9] R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).