Spectrochemical Study of Microscopic Crystals. V. Relation between Dichroism and Direct Interaction between Metal Atoms in the Crystals of Bis (Dimethylglyoximo)-Copper (II), Nickel (II) and Platinum (II)[1]

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In the earlier papers the present authors reported on the dichroism of those complex compounds which exhibit unusually deep colours in the crystalline state as compared with those in solution, and concluded that in the crystals of Magnus's green salt[2] and salts of tetracyanoplatinate (II)[3] there exists direct interaction between the central platinum atoms of planar complexes, which are arranged in such a way that they are piled one just above and below another. Recently Godycki and Rundle[4] reported on the crystal structure of bis (dimethylglyoximo)-nickel (II) and suggested the possibility of a direct, though weak, interaction between nickel atoms. They also asserted that the pleochroism of the crystal supported the above assumption, but gave no experimental value for the absorption coefficients. Moreover, their descriptions of the dichroism contradict our measurements, though the conclusion arrived at through their argument on the basis of their qualitative observation happens to be similar to ours. In this paper we report on the quantitative dichroism measurement of the crystals of bis (dimethylglyoximo)-copper (II), nickel (II) and platinum (II), and discuss the relation between the dichroism and the state of the complex molecules in these crystals.

Experimental

Materials. Bis (dimethylglyoximo) Copper (II) Black monoclinic prisms were obtained from solutions of copper acetate and of dimethylglyoxime in 50% alcohol. The crystal is remarkably dichroic; it appears to be dark reddish brown with linearly polarized light having its electric vector along the c-plane, the c-axis being the needle axis, and brownish yellow with that having its electric vector perpendicular to the c-plane. The Dichroism measurement was made with reference to the above two directions.

Bis (dimethylglyoximo) Nickel (II) The compound was prepared from an aqueous solution of nickel sulphate and an alcoholic solution of dimethylglyoxime, and recrystallized from chloroform. Red acicular crystals of orthorhombic system were obtained. A distinct dichroism was observed with a thin crystal under the microscope; the crystal appears red with linearly polarized light having its electric vector parallel to the needle axis, and orange with that having its electric vector perpendicular to the axis. The measurement was made in reference to these two directions.

Bis (dimethylglyoximo) platinum (II) Chocolate-coloured acicular crystals were prepared from an aqueous solution of potassium tetrachloroplatinate (II) and an alcoholic solution of dimethylglyoxime.[5] The crystal is strongly dichroic; it appears greenish black with the electric vector

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[1] Read before the meeting of the Symposium on Coordination Compounds, Nagoya, Japan, November 8, 1953.

[2] R. Tsuchida and S. Yamada, *J. Chem. Soc. Japan*, **70**, 44 (1949); S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951).

[3] S. Yamada, This Bulletin, **24**, 125 (1951).

[4] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 478 (1953).

[5] Gmelins Handbuch der anorg. Chem., 7. Aufl., Band 5, 1915, p. 604.

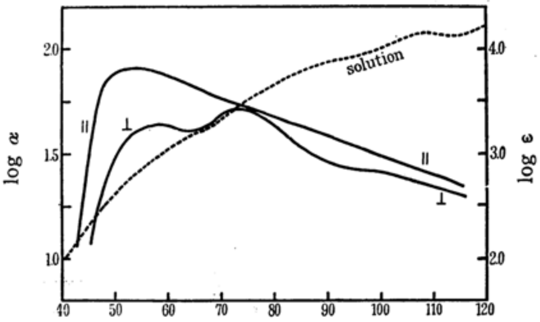
parallel to the needle axis, and orange with the electric vector perpendicular to the above. The dichroism measurement was per formed on the prism face in the above mentioned directions.

Measurements.—Quantitative dichroism measurement of the crystals was performed by the Tsuchida-Kobayashi's microscopic method.[6] α denotes absorption coefficient per mm. of a crystal. Molecular absorption coefficients of a crystal, k, were calculated from the relation, $k=10\alpha M/\rho$, where M and ρ represent molecular weight of the compound and density of the crystal, respectively.

Absorption spectra were obtained with a Beckman DU spectrophotometer in a chloroform solution of the nickel compound, and in an alcoholic solution of the copper compound. Extinction coefficients, ε, are given by the following expression, $\varepsilon=1/cd.\ \log(I_0/I)$.

∥-or ⊥-absorption means absorption of light with the electric vector parallel or perpendicular to the plane of the molecule, respectively.

Results and Discussion



Frequency (ν), 10^{13}/sec.

Fig. 1. Absorption spectra of bis (dimethylglyoximo) copper (II).

Bis (dimethylglyoximo) copper (II) Results of the measurement are shown in Fig. 1, and tabulated in Table I. The crystal structure analysis was reported by Bezzi et al.[7] According to their results, the planes of the planar molecules are parallel to each other and als to othe c-plane of the crystal. That is, the absorption spectrum with the electric vector along the c-plane corresponds to the ∥-absorption and the absorption with the electric vector perpendicular to the c-plane corresponds to the ⊥-absorption.

TABLE I

ABSORPTION MAXIMA OF BIS (DIMETHYLGLYOXIMO) COPPER (II)

	10^{13}/sec. ν	$\log\alpha$	k
∥-abs.	54	1.91	182×10^3
⊥-abs.	58	1.64	98×10^3

$\Delta\nu=4\times10^{13}$/sec., $\Delta\log\alpha_{\max}=0.27$, $\alpha_{\parallel}:\alpha_{\perp}=1.86:1$.

It has been known that complexes of copper (II), in general, show in the visible or infrared region an absorption band which can be ascribed to the linkages between the metal and the ligands. Comparing the absorption curves of copper-dimethylglyoxime with those of other cupric complexes, the band at $\nu=58\times10^{13}$/sec. (Band A) for the ⊥-absorption is considered as due to the linkages between copper and the ligands. Most metallic compounds with dimethylglyoxime or similar compounds,[8,9] which have π-electron system, exhibit absorption curves of complicated structure and also a band which can be supposed to be originated from dπ interaction between d-electrons of a transition metal atom and electrons of a ligand.[10] Thus the band at $\nu=73.2\times10^{13}$/sec. (Band B) is tentatively assumed to be of a similar nature to the above band associated with dπ interaction.

The ∥-absorption shows only a flat curve without a definite peak; it may be a superposition of the band A and band B.

With the absorption band A, the following regularity on the dichroism is obtained: *the ∥-absorption is bathochromic and hyperchromic to the ⊥-absorption.* The relation is similar to that which had been induced previously with planar quadri-coordinated complexes of transition metals,[11,12] and therefore can be understood in the same way as previously reported. Thus, since the electric moment associated with the linkage between copper and nitrogen atoms should be larger in the direction along the complex plane than in the direction perpendicular to the plane, ∥-absorption is expected to be hyperchromic to the ⊥-absorption. This was found to be the case with the cupric complex. Hence,

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

[7] S. Bezzi, E. Bua and G. Schiavinato, *Gazz. Chim. Ital.*, **81**, 856 (1951).

[8] Some of curves are found in Ref. 6, p. 194.

[9] Data with cobaltic compounds are given in H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, **1**, 11 (1951).

[10] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953), etc.

[11] About palladium (II) and platinum (II) complexes, see S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951); S. Yamada and R. Tsuchida, This Bulletin, **23**, 439 (1953).

[12] About cupric complexes, to be published later.

the dichroism indicates that the molecules in this crystal exist as independent units, in agreement with the result of the crystal structure analysis.[7]

Bis (dimethylglyoximo) nickel (II) Results of the measurement are shown in Fig. 2, and tabulated in Table II. According to the crystal analysis by Godycki et al.,[4] the planes of the complexes are parallel to each other and perpendicular to the c-axis, with the nickel atoms situated on lines along the c-axis. As in the case of the corresponding copper complex, it is supposed that the band of the ∥-absorption with its maximum at $\nu=60\times10^{13}$/sec. (Band A) is originated from transitions directly related to the linkages between the metal and the co-ordinating atoms, and that the band (Band B) with its maximum at $\nu=74\times10^{13}$/sec., which is reasonably considered as corresponding to the band at $\nu=86\times10^{13}$/sec. with the solution, may be due to the specific $d\pi$ interaction between the metal with d-electrons and atoms of the ligands with π-electrons. Instead of the two distinct bands in the ∥-absorption, only a broad absorption band is observed in the ⊥-absorption; in the latter both the bands would come so close together that only superposition of them may be observed. As to the band A, which has been assumed to be ascribed to the co-ordination linkages, there can be found the following relation: *the ⊥-absorption is by far hyperchromic to the ∥-absorption.* The relation is reverse to those observed with the corresponding copper compound, and also with metallic planar complexes of the normal type, that is, the type without the interaction between adjacent molecules.[11,12] The above relation that the electric vector perpendicular to the complex plane is more strongly absorbed than the vector along the plane indicates that the planar complexes are under some effect in the direction perpendicular to the planes of the complex molecules, and that the effect must be of such a nature as to cause a direct influence on the co-ordination linkages.

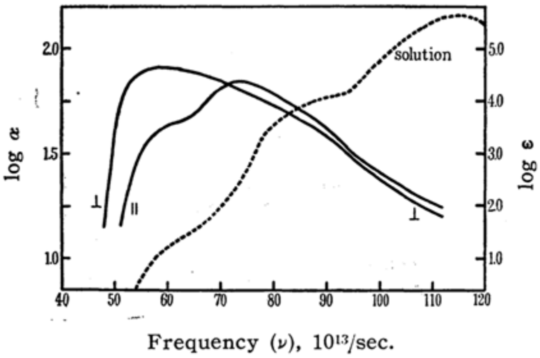

Fig. 2. Absorption spectra of bis (dimethylglyoximo) nickel (II).

TABLE II

ABSORPTION MAXIMA OF BIS (DIMETHYLGLYOXIMO) NICKEL (II)

	10^{13}/sec. ν	log α	k
∥-abs.	61	1.63	76×10^3
⊥-abs.	59	1.91	144×10^3

$\Delta\nu=2\times10^{13}$/sec., $\Delta\log\alpha_{\max}=0.28$, $\alpha_{\parallel}:\alpha_{\perp}=0.53:1$.

Such an effect would be considered to be a direct interaction between the nickel atoms which are arranged one just above and below another. Godycki et al.[4] also suggested, on the basis of their erroneous observation, similar interaction in this compound; their observation that the electric vector is more strongly absorbed along the plane of the complex than in the direction perpendicular to the plane is quite incomprehensible and seems incorrect.

Interactions between π-electrons might be considered besides the metal-metal interaction. However, since the complex molecules piled above and below one another are rotated about ninety degrees with respect to each other, the interaction between the π-electron systems of adjacent molecules may be ruled out. It is also probable that π-π interaction between the nitrogen atoms may contribute to this result to some extent, judging from the distance between nitrogen atoms of adjacent molecules. It seems reasonable, however, to consider that the motal-metal interaction should be dominant, compared with the contribution of the π-π interaction.

Bis (dimethylglyoximo) platinum (II) Results of the measurement are shown in Fig. 3. The crystal structure analysis of the compound has not been reported. However, judging from the crystal structure of the corresponding nickel and palladium compounds,[4] it is probably certain that the complex planes in the platinum (II) compound are parallel to each other and perpendicular to the needle axis, just as in the case of the other two. On the basis of the above assumption was assigned the ∥-and ⊥-absorp-

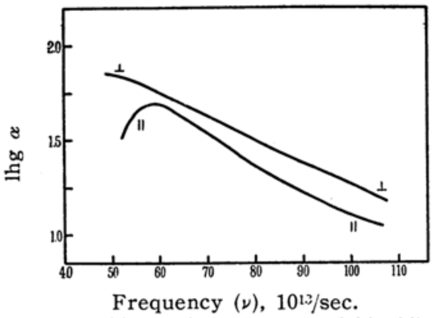

Fig. 3. Absorption spectra of bis (dimethylglyoximo) platinum (II).

tion. Since the ⊥-absorption stretches out beyond the region of measurement, the maximum could not be determined. It is seen that the crystal of the platinum-dimethylglyoxime compound shows its absorption in the extraordinarily long wave-length region, in comparison with other platinum compounds such as potassium tetrachloro-, tetrabromo-,[11,13] and dioxalato-[14] platinate (II), and others. This suggests that some effect might be exerted upon the planar molecules in the former compound. Further, by inspecting the dichroism, the following relation is found: *the ⊥-absorption is much more hyperchromic and bathochromic than the ∥-absorption.* The above relation is reverse to that in case of complexes of the normal type. The reversal of the effect as to the dichroism indicates that the effect, which has direct influence on the absorption closely connected with the linkages between the metal and the ligands, should be taken into consideration. Hence, as in the case of the corresponding nickel compound, a direct interaction is supposed to exist between platinum atoms.

The Nature of the Metal-Metal Interaction The metal-metal interaction as proposed in the nickel-and platinum-dimethylglyoxime compounds is considered to be of a similar nature to the interaction which was previously reported by the present authors in the case of Magnus's green salt[2] and salts of tetracyano-platinate (II).[3] In order to explain the metal-metal interaction in the latter crystals, the following assumption was presented in the former report.[2,3] In the quadri-coordinated planar complexes of platinum (II), four atoms of the ligands with two pairs of electrons around the central metal form octahedral hybridization.[15] The pairs of electrons above and below platinum cores of the complexes exert mutual effects upon one another, overlapping of electronic density being naturally expected (Fig. 4).

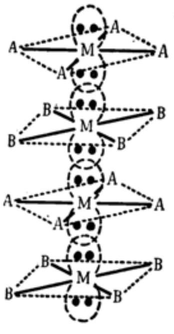

Fig. 4. Metal-metal interaction in the Magnus's type compounds.

The same assumption may apply to the crystal of the nickel (II)-and platinum (II)-dimethylglyoxime compounds. When the above metal-metal interaction is getting stronger, the overlapping of the electrons may also become larger. In other words, the greater the overlapping of the electrons, the more the sharing of electrons. In the extreme structure, in which the overlapping might reach the extremity, complete sharing of electrons might happen (Extreme structure II in Fig. 5).[16] It may be reasonably supposed that the more stable the extreme structure, the larger would be the overlapping and the greater the contribution of the structure would result, in which sharing of the electrons is complete. It is to be noted that the metal-metal interaction of the said type has been found mostly with the compounds

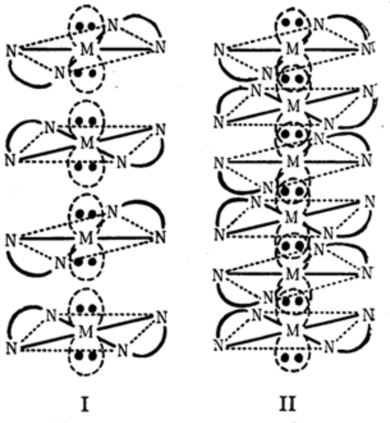

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Fig. 5. Extreme structures of some metallic dimethylglyoximo compounds involving metal-metal interaction.

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[13] S. Yamada, H. Yoneda and R. Tsuchida, *J. Chem. Soc., Japan*. **69**, 145 (1948).

[14] R. Tsuchida and S. Yamada, unpublished.

[15] About the possibility of octahedral hybridization in quadri-coordinated planar complexes, see, for example, R. Tsuchida, M. Kobayashi and H. Kuroya, *Rev. Phys. Chem. Japan*, **13**, 158 (1939).

[16] The contribution of the extreme structure, in which complete sharing of an electron pair occurs, was recently pointed out by Godycki et al. (Ref. 4).

of Ni (II), Pd (II) and Pt (II). In order to explain such tendency, we wish to propose the following hypothesis: *When complete sharing of electrons would occur between complex molecules arranged above and below one another (structure II), Ni (II), Pd (II) and Pt (II) would attain the effective atomic number of the rare gases and thereby the extreme structure II (Fig. 5) might be stabilized.* Thus the larger contribution of the extreme structure II, and hence the greater stability of the metal-metal interaction, could be explained in terms of the above hypothesis with Ni (II), Pd (II) and Pt (II) compounds.

The same assumption applies satisfactorily also to the stability of the molecule of copper acetate, $Cu_2(CH_3CO_2)_4 \cdot 2H_2O$,[17] in which, according to the above hypothesis, the copper atoms in the extreme structure would attain the effective atomic number of krypton by sharing one pair of electrons between two copper atoms.

Summary

Dichroism of the crystals of bis (dimethylglyoximo)-copper (II), nickel (II) and platinum (II) has been quantitatively determined by the microscopic method in the region from 2400 to 7000 Å.

The crystal of the copper compound has been found to show dichroism of the normal type, indicating that no specific metal-metal interaction can be expected in this crystal.

The crystals of the nickel (II) and platinum (II) compounds exhibit anomalous dichroism. It has been concluded that in these crystals there should exist metal-metal interaction.

A hypothesis has been presented, in order to explain the tendency that the specific metal-metal interaction similar to that proposed above has been found mostly with Ni (II), Pd (II) and Pt (II) compounds.

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[17] About the configuration of the molecule, see J. N. van Niekerk and F. R. L. Schoening, ***Acta Cryst.***, **6**, 227 (1953).