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Characterization of Oxalatodiammineplatinum(II) Twins under the Conoscope

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The results of optical studies on oxalatodiammineplatinum(II) are presented and interpreted, particularly because it affords an example of contact twinning with an optic axis normal to the composition plane. The composite interference figures resulting from this arrangement are well-defined and characteristic.

This compound provides another case in which there is discrepancy between the actual sign of birefringence and the sign deduced from the present theory for the origin of birefringence in planar complexes.

Incidental to a study of substitution reactions of molecular platinous coordination compounds, oxalatodiammineplatinum(II) was prepared and properties suitable for its quick and easy characterization were investigated. It was observed that the interference figures from some of the crystals in a random field behaved in a strikingly unusual fashion. This behavior was reproduced in subsequent preparations and was found to be diagnostic of the case of contact twinning in which an optic axis is normal to the composition plane. Though the crystals obtained were too small for goniometric measurement, the relations between morphology and optical properties were adequately established by study under the conoscope.

Crystallographic properties

The colorless needle-like product, 0·2–0·6 mm. in length and up to 0·025 mm. in width, was assumed to be pure on the basis of milligram-scale analyses for nitrogen and platinum. Some of the acicular crystals showed a centered biaxial optic axis figure with the acute bisectrix direction parallel to the elongation. These figures behaved normally in all respects and permitted evaluation of the birefringence as strong and positive, $2V$ as approximately 70° (from the curvature of the isogyre), the dispersion ($r > v$), and the β refractive index. When such crystals as these were rolled 90° in a mount of viscous Canada balsam, they gave a diffuse but recognizable optic normal figure from which it could be judged that Bx_a lay approximately parallel to the traces of the end faces. In this orientation the end faces made an acute angle of 56° with the elongation and the crystals extinguished completely at an acute angle of +34° between the fast vibration direction (Bx_o) and the elongation or c axis. Since an optic axis was perpendicular to c and $Bx_a \frown c = -56°$, the optic axial angle was known accurately enough, without direct measurement, to permit calculation of the γ refractive index from values of the α and β indices measured by the immersion method. These observations and measurements were sufficient to determine the crystallographic properties of single crystals given in Table 1.

Table 1. *Crystallographic properties of oxalatodiammineplatinum(II)*

Crystal system: monoclinic, $\beta = 124°$.
Habit and forms: needles elongated parallel to c, showing orthopinacoid {100} and bladed clinopinacoid {010}; commonly exhibits contact twinning on (100) and parallel growths on (010).
Optic axial plane: 010 ($Y = b$).
Extinction: $X \frown c = 34°$ in obtuse angle β.
Acute bisectrix: Z (birefringence positive).
Optic axial angle (derived as noted in the text): $2V \sim 68°$.
Refractive indices at 26° C.: $\alpha_D = 1{\cdot}612 \pm 0{\cdot}005$, $\beta_D = 1{\cdot}670 \pm 0{\cdot}005$, $\gamma_D = 1{\cdot}83 \pm 0{\cdot}02$; $\gamma - \alpha = 0{\cdot}21$.
Dispersion: slight, inclined, $r > v$.

Other crystals in random fields remained quite uniformly illuminated during rotation in parallel light between crossed polarizer and analyzer but gave optic axis figures which were variously distorted and tended towards the 'maximum abnormality' shown in the series of lettered photographs of Fig. 1. In the parallel positions the isogyre was well-defined and appeared normal, but the darkness and ellipticity of the first ring showed that the figure was not pure. During rotation of the stage from the parallel position (A) to the 45° position (B), the ends of the isogyre disappeared along with the segments of the first ring in the NW and SE quadrants, and then the remainder separated into dark, well-defined arcs located in the NE and SW quadrants, the region which would have been crossed by a normal isogyre. Further rotation to the parallel position (C) resulted in reforming of the ring and reappearance of the complete isogyre vertically. Photos (D), (E) and (F) give black-and-white indications of the colored appearances at 22°, 45° and 68° in the second quadrant. The same orientations were studied in eight bands of the visible spectrum, from red to blue, as isolated by means of appropriate Wratten filters. There were no important differences

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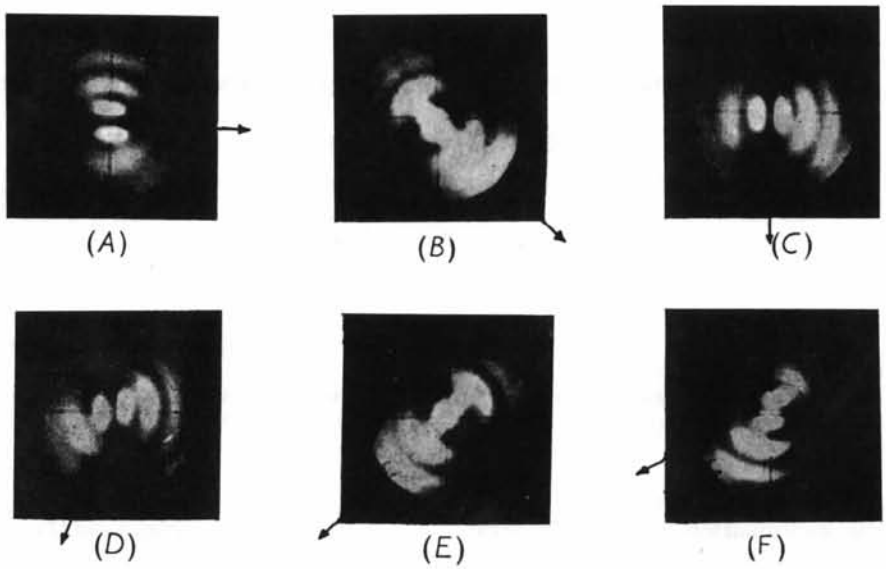


Fig. 1. Abnormal interference figures given by contact twin of oxalatodiammineplatinum(II) when the composition plane is normal to the conoscope axis and when the optic axial plane lies: (*A*) parallel to the horizontal crossline, 1st and 4th quadrants; (*B*) at 45° to a crossline, 1st quadrant; (*C*) parallel to the vertical crossline, 1st and 2nd quadrants; (*D*), (*E*) and (*F*) at 22°, 45° and 68° in the second quadrant. (Arrow indicates center direction of the reference circle with quadrants numbered as sketched.)

1	2
4	3

The specimen was not rolled quite 90° from the view diagrammed in Fig. 2 and consequently the photographs show slight inclination of the optic axis.

from the deportment of the isogyre and first ring in white light.

Still other acicular crystals in randomly-oriented fields showed the outlines diagrammed in Fig. 2. They proved to be contact twins, 10–15 microns wide, with extinction angles symmetrical about the composition plane (100), slow directions parallel to (001), and of orientation giving a confused flash figure. Some of the twins were composed of individuals showing uniform, low-order polarization colors; when rolled 90° and measured, they were found to be 2–3 microns thick. Others exhibited high-order whites and, when rolled 90° for the view normal to the composition plane, gave centered optic-axis figures which exhibited the abnormal behavior described above. Close inspection of the (010) faces revealed what appeared to be layer boundaries paralleling the ends and focusing-out in order, for example from bottom to top as the focus was raised. The horizontal distance between each of the boundaries was less than a micron but it was possible to prove that the colors between them increased in order towards that of the face and that all were extinguished at the same angle as the face. When the width of the (100) face was measured and divided by the number of layer boundaries, the result fell in the range 2–3 microns. The trace of the boundaries parallel to *c* could be followed by precise focusing as these twins were rolled towards the (010) view.

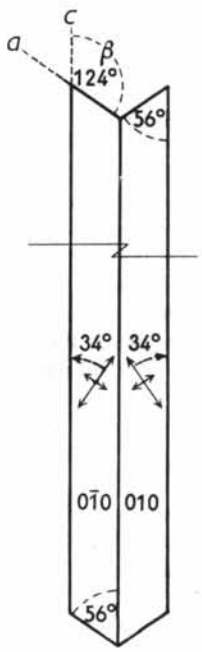


Fig. 2. Diagrammatic representation of a single contact twin of oxalatodiammineplatinum(II) showing (010) and the trace of the composition plane. $Z = Bx_a$ is indicated by the shorter arrow, $X = Bx_o$ by the longer arrow.

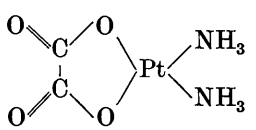
Thus it became evident that the twins which were thick enough to permit convenient study of their optic-axis figures were made up of laminae similarly-oriented and stacked at right angles to the composition plane. The abnormal optic-axis figures were obtained when a laminated twin was viewed normal to the composition plane, the 'degree of abnormality' being dependent on the relative widths of the twin in-

dividuals. This explanation was neatly confirmed by the figures obtained from a specimen which had been cleaved part way along the length parallel to the composition plane.

Discussion

When an interference figure is obtained from two superposed crystals, it is a composite of the two superposed figures. If the two crystals are oriented at random with respect to each other, the resulting figures are not useful. On the other hand, if the two crystals are related as twinned units, the composite figures may be well-defined and highly characteristic. For the above particular case of viewing along an optic axis, normal to the composition plane, the parallel positions give a nearly normal biaxial figure because the isogyres of the separate figures are superposed. However, the opposite direction of Bx_a in the two halves of the twin becomes very apparent during rotation to intermediate positions. The isogyres move from superposition and each is rendered invisible by the double refraction of the other individual except where subtraction of retardation is complete. Wood (1951) has interpreted a case of abnormal figures resulting from the combination of laterally-displaced bisectrix figures.

Since the optical properties of a crystal are the result of its structure, it should be possible, conversely, to gain from them a general idea about the arrangement of the structural units in the crystal if the units are polyatomic and are the main source of the crystal's refractivity. Valuable correlations in this respect have been established by comparisons of crystal optics and structures. These qualitative relationships, summarized by Hartshorne & Stuart (1950), are also intuitively satisfactory when considered in the light of the usual ideas about interaction between electromagnetic radiation and the electronic atmospheres of molecules. However, the case of oxalatodiammineplatinum(II) presents a disturbing anomaly in the positive character of its birefringence. X-ray analysis of monoclinic oxalatodiamminepalladium(II) led Mann, Crowfoot, Gattiker & Wooster (1935) to conclude that the length of the molecule lay along a and the width along b so that it was bisected by the crystallographic plane of symmetry which was also the optic axial plane. Accordingly, it would be predicted that the molecular planes of the isomorphous platinum complex



also would parallel the $a\,b$ plane and, therefore, that the β index as well as well as γ would be much larger than α, resulting in strong but negative birefringence.

Mellor (1943) summarizes optical data on square planar platinous complexes and finds that all exhibit strong double refraction. He also points out that, for all except three of the compounds, the sign is negative. These three, which are hydrated tetracyanoplatinites, are considered to have structures analogous to the known structure of isomorphous $Ba[Pt(CN)_4].4\,H_2O$, and, accordingly, should be optically negative.

These discrepancies between the actual sign of birefringence and the sign deduced from the postulate for the origin of birefringence in planar complexes emphasize the limitations of the theory in its present form.

Experimental

Oxalatodiammineplatinum(II) was obtained in high yield by treating a saturated aqueous solution of 30 mg. of *cis*-dichlorodiammineplatinum (II) (Jorgenson, 1900) with a ten times excess of potassium oxalate. The product crystallized slowly during days of standing at room temperature. It was filtered, washed with ice-cold water and finally ethanol, and dried *in vacuo*. On a microscope hot stage, decomposition began at 195° C. and was complete below 208° C. when the temperature was raised at the rate of 1° C. per minute. Grünberg (1931) prepared this compound from the dichloro complex by making the dinitrato compound and heating the latter in solution with excess oxalic acid at 100° C. for 1–2 hr. The higher decomposition temperature recorded (230° C.) could be accounted for by a faster heating rate and/or different method of observation.

Analysis: Calculated for $PtN_2H_6C_2O_4$: Pt, 61·53; N, 8·83. Found: Pt, by ignition, $61{\cdot}5_0$; N, by Dumas, $8{\cdot}7_5$.

All optical properties were determined in white light unless otherwise noted. Since extinction was sharp and a determination of the α index in white light fell within the precision limits given for α_D, the value for $2V$ derived from the extinction angle could be used for calculation of the γ index.

Several estimations of the birefringence were made by measuring the thickness and retardation exhibited by (010) of single crystals. A typical determination gave retardation = 470 m.μ by calibrated quartz wedge, width of (100) = 2μ by calibrated Filar micrometer after rolling from the view of (010), and birefringence = 0·25 from the Michel–Levy chart.

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