354. *The Planar Configuration for Quadricovalent Nickel, Palladium, and Platinum : Dithio-oxalate Derivatives.*

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It is now definitely established that bivalent nickel, like palladium and platinum, exhibits a planar distribution of valencies in normal quadricovalent compounds (see, *e.g.*, Cox, Pinkard, Wardlaw, and Webster, this vol., p. 459), and it is therefore to be expected, since their atomic diameters are not greatly different, that isomorphism should exist between

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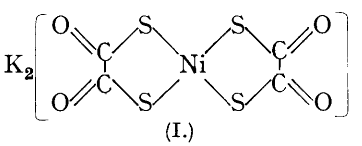
* *I.e.*, a value obtained from dipole moment determinations in solution. If the larger value, 1·7, be employed in the calculations instead (cf. McAlpine and Smyth, *J. Chem. Phys.*, 1935, **3**, 55), the angle becomes slightly greater (*viz.*, 77°) but the above argument is not affected thereby.

corresponding compounds of these metals. Brasseur, de Rassenfosse, and Piérard (*Z. Krist.*, 1934, **88**, 210) have shown that the three hydrated double cyanides with barium are isomorphous, but the presence of water of crystallisation makes it uncertain whether the complex ion in these salts is truly four-covalent. We now find that the anhydrous potassium nickelodithio-oxalate (I) is completely isomorphous with the corresponding palladium and *platinum* compounds, the latter of which we have prepared for the first time. This discovery is of considerable importance from the point of view of the X-ray investigation of co-ordination compounds. It has been possible in previous studies, chiefly from considerations of symmetry, to establish the planar configuration of the metal atom, but owing to the preponderating effect of the central atom over the attached groups (consisting usually of carbon, nitrogen, and oxygen atoms), the determination of the complete structure by means of intensity measurements has been a matter of great difficulty. In the present case, however, the sulphur atoms and potassium ions have a scattering power in the aggregate comparable with the metal atom, and in addition, comparison of the three compounds makes it possible to estimate the relative contribution of the metal atom and the chelate groups to the structure factor of any lattice plane. As a result we have been able to determine with reasonable accuracy (apparently for the first time for a chelated compound) the positions of all the atoms in the crystal lattices of these salts.



(I.)

The crystals are monoclinic, and X-ray investigation shows that the unit cell contains four molecules, the space-group being $A2/a$ (C^6_{2h}). The complex ion thus possesses either a two-fold axis or a centre of symmetry; the latter alternative would definitely require the four metal valencies to be coplanar, whereas either a planar or a tetrahedral configuration would be consistent with two-fold axial symmetry. Consideration of the intensities of {100}, however, shows immediately that all the atoms in the molecule are coplanar. For all three substances, the (200) reflexion is very intense, while the fourth- and sixth-order intensities fall off normally; these facts, combined with the good cleavage parallel to {100}, strongly suggest flat molecules lying in the (200) planes. We have estimated carefully the relative intensities of the three orders, and have further, by comparison with the (200) reflexion from rock-salt, estimated the *absolute* intensities of the nickel reflexions. Since the linear absorption coefficient of copper K_α radiation is the same in rock-salt and potassium nickelodithio-oxalate, these comparisons could be made with reasonable accuracy. The observed intensities for the nickel compound are given below (col. 2), that for the (200) rock-salt reflexion being taken as 100. The remaining columns contain intensities calculated for various possibilities : (*a*) all the atoms lying in the (200) plane; (*b*) all the atoms of the complex ion lying in the (200) planes, the potassium ions interleaving them; (*c*) tetrahedral complex ion, its longest direction lying in the (200) plane, potassium ions in the same plane. [Other arrangements of a tetrahedral ion are possible, but they lead to figures in no better accord with experiment than those in column (*c*) below.]

Plane.	Observed intensity.	Calculated intensity. (*a*).	(*b*).	(*c*).
200	160	145	45	9
400	34	29	29	0
600	7·5	10·5	3	6

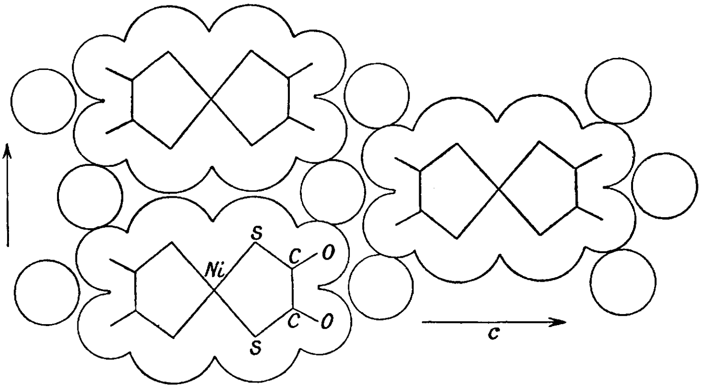
It is quite clear that the only structure which is in agreement with the experimental results is that in which all the atoms are coplanar, and in the (200) planes; no other structure can explain the high absolute intensity of the (200) reflexion. The absolute intensities of the palladium and platinum compounds are more difficult to measure, but the complete agreement between the relative intensities for all three substances shows that the structure is the same throughout, as indeed is to be expected from their isomorphism. It may therefore be accepted that in all three cases the complex ions are completely flat and, together with the potassium ions, lie in the (200) planes.

It is next necessary to determine whether the metal atoms lie in the two-fold axes or on the centres of symmetry. In the former case their positions are determined by one parameter *u*, and the orientation of the complex ions is confined by symmetry considerations to two possibilities, whereas if the ions are centro-symmetrical their centres are fixed but their orientations are unrestricted. Consideration of the cell dimensions, however, shows that a further restriction must be introduced; it is clear that the greatest length of the complex ion must be nearly parallel to the *c*-axis (22·65 Å.) on account of the shortness of *b* (7·56 Å.). Now, four equivalent symmetry centres may have co-ordinates

(*a*) (0,0,0), ($\frac{1}{2}$,0,0), (0,$\frac{1}{2}$,$\frac{1}{2}$), and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$)
or (*c*) (0,0,0), ($\frac{1}{2}$,0,$\frac{1}{2}$), ($\frac{1}{2}$,$\frac{1}{2}$,0), and (0,$\frac{1}{2}$,$\frac{1}{2}$)

(see, *e.g.*, Wyckoff, " Analytical Expression of the Results of the Theory of Space Groups ").

Since the complex ions must be nearly parallel, and have heavy atoms at their centres, either of the above arrangements would be indicated by weak odd-layer lines in appropriate photographs—*a*-axis in case (*a*), [101] in case (*c*). This is not observed, and moreover, no arrangement of the complex ions on the symmetry centres has been found adequate to account for the observed intensities of {010}. We conclude that the metal atoms lie on the two-fold axes, their co-ordinates being ($\frac{1}{4}$,u,0), ($\frac{3}{4}$,$\bar{u}$,0), ($\frac{1}{4}$, $\frac{1}{2} + u$,$\frac{1}{2}$) and ($\frac{3}{4}$,$\frac{1}{2} - u$,$\frac{1}{2}$). The orientation of the complex ions is now fixed, since of the two possible arrangements having two-fold symmetry, only that in which the carbon–carbon bonds are parallel to the *b*-axis (see fig.) is consistent with the cell dimensions. The value of the parameter *u* is readily determined; it is found that {010} is quartered, and the fact that this quartering occurs for all three compounds shows that the metal atoms themselves must lie on the (040) planes—*i.e.*, *u* = 0·125.



Planar configuration of quadrivalent platinum, palladium, and nickel dithio-oxalate derivatives.

The positions and orientation of the complex ions as a whole having been found, it remains to determine the positions of the individual atoms in the chelate groups. In order to simplify this task, we have assumed that, as far as atomic positions are concerned, the complex ion is symmetrical about the line joining the centres of the carbon–carbon bonds (as well as about the *b*-axis). We have further assumed that the carbon–carbon and carbon–oxygen distances are 1·54 Å. and 1·14 Å. respectively, and that the angle between single carbon bonds is 109°; the last two values are those found recently from a study of benzoquinone (Robertson, *Proc. Roy. Soc.*, *A*, 1935, **150**, 106). We have then adjusted the position of the sulphur atoms and potassium ions to give the best agreement with the observed intensities, and the fig. shows the arrangement of the molecules in the (200) plane finally deduced in this way; the molecules in the next parallel (200) plane have the same relative arrangement but are displaced a distance 0·25*b* along the *b*-axis relative to the first layer, and if projected on the first layer are displaced a distance $\frac{1}{2}a$ cos β parallel to the *c*-axis.

The figure may be taken to represent the structure of any of the three compounds, the only important difference between them being in the metal–sulphur distance, which is rather less for the nickel compound than for the other two. The following table shows the agreement between various observed and calculated intensities for the platinum compound. The optical properties of the crystals afford further confirmation of the general correctness of the structures; the birefringence is extremely high, the maximum index being parallel to the *c*-axis, and the minimum perpendicular to (100).

	Intensity.			Intensity.			Intensity.	
Plane.	Calc.	Obs.	Plane.	Calc.	Obs.	Plane.	Calc.	Obs.
200	605	560	060	0	0	$12,0\bar{2}\bar{4}$	24	23
400	137	137	002	72	90	$20\bar{6}$	34	45
600	52	27	008	3	0	$40\bar{1}\bar{2}$	24	23
020	0	0	$40\bar{8}$	100	90	$80\bar{1}\bar{2}$	24	23
040	94	70	$80\bar{1}\bar{6}$	0	0	$30\bar{1}\bar{0}$	22	18

The complete structure is defined by the atomic co-ordinates as follows:

(*a*) *Platinum and palladium derivatives.*

Pt (or Pd)	$(\frac{1}{4},\frac{1}{8},0)$ $(\frac{3}{4},\overline{\frac{1}{8}},0)$ $(\frac{1}{4},\frac{5}{8},\frac{1}{2})$ $(\frac{3}{4},\frac{3}{8},\frac{1}{2})$		
K	$(0\cdot250,0\cdot125,0\cdot288)$	$(0\cdot750,\overline{0\cdot125},0\cdot288)$	$(0\cdot250,0\cdot625,0\cdot788)$
	$(0\cdot750,0\cdot375,0\cdot788)$	$(0\cdot250,0\cdot125,\overline{0\cdot288})$	$(0\cdot750,\overline{0\cdot125},\overline{0\cdot288})$
	$(0\cdot250,0\cdot625,0\cdot212)$	$(0\cdot750,0\cdot375,0\cdot212)$	

The co-ordinates of the atoms in the chelate groups attached to the platinum (or palladium) atom at $(\frac{1}{4},\frac{1}{8},0)$ only are given below; those for the others are readily derived by appropriate translations, since all the complex ions are parallel.

S	$(0\cdot250,0\cdot363,0\cdot072)$	$(0\cdot250,\overline{0\cdot113},0\cdot072)$	$(0\cdot250,0\cdot363,\overline{0\cdot072})$
	$(0\cdot250,\overline{0\cdot113},\overline{0\cdot072})$.		
C	$(0\cdot250,0\cdot225,0\cdot137)$	$(0\cdot250,0\cdot025,0\cdot137)$	$(0\cdot250,0\cdot225,\overline{0\cdot137})$
	$(0\cdot250,0\cdot025,\overline{0\cdot137})$		
O	$(0\cdot250,0\cdot294,0\cdot182)$	$(0\cdot250,\overline{0\cdot044},0\cdot182)$	$(0\cdot250,0\cdot294,\overline{0\cdot182})$
	$(0\cdot250,\overline{0\cdot044},\overline{0\cdot182})$		

(*b*) *Nickel derivative.*

Ni and K the same as Pt and K respectively above.

S	$(0\cdot250,0\cdot360,0\cdot063)$	$(0\cdot250,\overline{0\cdot110},0\cdot063)$	$(0\cdot250,0\cdot360,\overline{0\cdot063})$
	$(0\cdot250,\overline{0\cdot110},\overline{0\cdot063})$		
C	$(0\cdot250,0\cdot224,0\cdot130)$	$(0\cdot250,0\cdot026,0\cdot130)$	$(0\cdot250,0\cdot224,\overline{0\cdot130})$
	$(0\cdot250,0\cdot026,\overline{0\cdot130})$		
O	$(0\cdot250,0\cdot292,0\cdot175)$	$(0\cdot250,\overline{0\cdot042},0\cdot175)$	$(0\cdot250,0\cdot292,\overline{0\cdot175})$
	$(0\cdot250,\overline{0\cdot042},\overline{0\cdot175})$		

The principal interatomic distances are Ni–S = 2·30, Pd–S = 2·44, Pt–S = 2·44, and C–S = 1·83 Å., and the valency angle of the sulphur atoms is within 2° of the tetrahedral angle. The above value of the Pt–S distance agrees reasonably well with the value 2·32 Å. found in platinous sulphide (Bannister, *Min. Mag.*, 1932, **23**, 188).

The K–O distance varies between 2·57 and 3·0 Å., and the minimum K–S distance is 3·73 Å. The closest distance of approach of atoms in different complex ions is 3·2 Å.

In conclusion, it may be pointed out that in this series of investigations 14 four-co-ordinated derivatives of bivalent platinum, palladium, or nickel have now been shown to possess a planar configuration; in view of the diverse nature of the compounds studied, there can be no doubt that this configuration is quite general, and can only be modified in very special cases such as may occur with ter- or quadri-dentate chelate groups.

EXPERIMENTAL.

Potassium Dithio-oxalate.—This salt was prepared according to the method of Jones and Tasker (J., 1909, **95**, 1904).

Potassium Nickelodithio-oxalate.—Concentrated aqueous solutions of nickel sulphate (2 g. in 10 ml.) and potassium dithio-oxalate (2 g. in 4 ml.) were mixed at room temperature; a deep purple solution was at once produced, from which small, almost black crystals separated. On recrystallisation from hot water, large iridescent bipyramids were obtained [Found: Ni, 15·5; C, 12·8. Calc. for $K_2Ni(COS)_4$: Ni, 15·6; C, 12·7%]. By allowing the solution to crystallise at 0°, some needles were sometimes obtained together with the bipyramids, but in no case was the needle form obtained alone, as would occur if the substance were dimorphous, as reported by Robinson and Jones (J., 1912, **101**, 62).

Potassium Palladodithio-oxalate.—To a solution of potassium chloropalladite (1 g. in 25 ml. of water) was added an aqueous solution of potassium dithio-oxalate (1·1 g. in 5 ml.). Orange-yellow bipyramids of the palladium derivative separated [Found: Pd, 25·4; K, 18·1; C, 11·4. Calc. for $K_2Pd(COS)_4$: Pd, 25·1; K, 18·3; C, 11·3%].

Potassium Platinodithio-oxalate.—An aqueous solution of potassium dithio-oxalate (1 g. in 5 ml.) was added to a solution of potassium chloroplatinite (1·2 g. in 20 ml.), and the mixture kept for a few hours. Dark red crystals of *potassium platinodithio-oxalate* slowly separated and were recrystallised from water [Found: Pt, 38·1; K, 15·7; C, 9·3. $K_2Pt(COS)_4$ requires Pt, 38·1; K, 15·2; C, 9·3%].

Crystallography.—Crystallographic data for the nickel derivative (I) were obtained by Hallimond (Robinson and Jones, *loc. cit.*), who described it as monoclinic prismatic with axial ratios $a:b:c = 1{\cdot}7637:1:2{\cdot}8664$; $\beta = 109°\ 04'$, the forms observed being $p\{111\}$ and $s\{\bar{1}11\}$ equally developed, with $a\{100\}$ very small. Cleavage was found to be perfect on a and imperfect on $b\{010\}$; density 2·13 g./c.c. The palladium derivative was obtained, but no crystallographic data were recorded. The crystals prepared for the present work corresponded completely with this description; the palladium and platinum derivatives were closely similar, exhibiting the same forms and cleavages. It is convenient to re-allot indices according to the scheme $\dfrac{a(100)\ \ p(111)\ \ s(\bar{1}11)}{a(100)\ \ o(1\bar{1}\bar{1})\ \ p(0\bar{1}1)}$ so that Hallimond's elements for the nickel derivative become $a:b:c = 1{\cdot}417:1:2{\cdot}866$; $\beta = 143°\ 52'$.

The cell dimensions and space-groups were determined by means of single-crystal rotation and oscillation photographs with copper K_α radiation, the results being:

$K_2Ni(COS)_4$: $a = 10{\cdot}99$, $b = 7{\cdot}80$, $c = 22{\cdot}23$ Å.; $\beta = 144°\ 01'$; $a:b:c = 1{\cdot}409:1:2{\cdot}850$; number of molecules in the unit cell $(n) = 4$, d (calc.) $= 2{\cdot}23$ g./c.c. (obs. 2·17). Missing reflexions: $\{hkl\}$ halved for $(k + l)$ odd, all $\{h0l\}$ halved, whence the space-group is $A2/a(C_{2h}^6)$ and the molecular symmetry either 2 or $\bar{1}$.

$K_2Pd(COS)_4$: $a = 11{\cdot}13$, $b = 7{\cdot}78$, $c = 22{\cdot}56$ Å.; $\beta = 144°\ 05'$; $a:b:c = 1{\cdot}430:1:2{\cdot}900$; $n = 4$; d (calc.) $= 2{\cdot}46$ g./c.c. (obs. 2·40); space-group $A2/a$; molecular symmetry 2 or $\bar{1}$.

$K_2Pt(COS)_4$: $a = 11{\cdot}16$, $b = 7{\cdot}63$, $c = 22{\cdot}62$ Å.; $\beta = 144°\ 04'$; $a:b:c = 1{\cdot}462:1:2{\cdot}965$; $n = 4$; d (calc.) $= 3{\cdot}01$ g./c.c. (obs. 2·94); space-group $A2/a$; molecular symmetry 2 or $\bar{1}$.

These results demonstrate conclusively the complete isomorphism of the three derivatives. X-Ray photographs showed that the needle-shaped crystals of the nickel derivative possess the same structure as the normal bipyramidal crystals, being elongated along the c-axis and bounded by the cleavage forms a and b.

Intensity Measurements.—As the crystals were scarcely large enough to be examined on the ionisation spectrometer, the procedure adopted in comparing the intensities of two reflexions was to record them on one photograph, the stronger one being reduced by absorbing screens of aluminium foil until approximately equal (on the photograph) to the weaker one. The equality of the two reflexions could be judged by eye to about 10%, while the reduction due to the known thickness of aluminium foil could be calculated very accurately. Hence the relative intensities measured are accurate to about 10%. To obtain the absolute intensities of the nickel reflexions, they were compared with the $\{200\}$ reflexions from rock-salt, no correction for absorption being necessary, since the linear absorption coefficients for copper K_α radiation are respectively 155 and 162 cm.$^{-1}$. The rock-salt crystal and the nickel derivative crystal used were of the same shape and approximately the same size, the crystals being measured under the microscope and a correction made for the slight difference in volume. As a two-crystal spectrometer was not available, the rock-salt and the dithio-oxalate crystal were photographed successively. To obtain uniform exposures, the X-ray tube (a Metalix tube run with half-wave rectification) was run under as steady conditions as possible, the actual exposure being determined by a prepayment meter of the ordinary type in the primary circuit of the H.T. transformer. Careful and repeated tests showed that this procedure could be relied upon to give *X*-ray exposures reproducible within less than 5% ; the final absolute intensities for the nickel derivative are considered to be accurate within 10%, apart from any errors due to extinction. No allowance for extinction has been made, and in measuring the absolute intensities, the standard sodium chloride intensities have been calculated directly, James and Brindley's ionic scattering factors (*Z. Krist.*, **1931**, **78**, 470) being used. This is equivalent to assuming that the extinction corrections are the same for rock-salt and for the nickelodithio-oxalate; the general character of the reflexions from the latter shows that the crystals are of a similar degree of imperfection to rock-salt, and in the actual experiments freshly cleaved fragments of both were used.

In making the calculations of intensities for the proposed structure the atomic scattering factors (f) of James and Brindley (*loc. cit.*) were used, the geometrical structure factors (F) being calculated in the usual way, so that

$$I_{(\mathrm{calc.})} = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot \left(\frac{\text{density}}{\text{mol. wt.}} \; \Sigma F \, . \, f\right)^2$$

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