95. *The Stereochemistry of Quadricovalent Atoms: Gold.*

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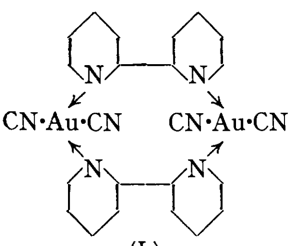
The quadricovalent aurous compounds $K[Au(CN)_2dipy]$ and $M^I[Au(CN)_2phenan]$ (M^I = K, Tl, NH_4) have been prepared, generally by the action of 2 : 2′-dipyridyl (dipy) or *o*-phenanthroline (phenan) on the double aurous cyanides, $M^IAu(CN)_2$. The effective atomic number of the gold atom in these compounds is 86—that of radon—and a tetrahedral distribution of valencies round the aurous atom would be expected. An *X*-ray analysis has shown that the molecule of $K[Au(CN)_2dipy]$ possesses a two-fold axis of symmetry; the occurrence of a short axis (3·74 A.) eliminates the possibility of a tetrahedral configuration, and it is inferred that the four valencies of the aurous atom in this compound are coplanar (or nearly so). The *X*-ray data also indicate a planar configuration in $K[Au(CN)_2phenan]$. These compounds thus provide an exception to the generalisation that a quadricovalent atom possessing the effective atomic number of a rare gas has a tetrahedral valency distribution.

Striking examples of a change of configuration with change in the principal valency of the central quadricovalent atom have been disclosed in recent investigations of co-ordination compounds of copper, silver, and thallium; for example, in quadricovalent compounds of univalent copper and univalent silver, the four bonds to the cuprous and argentous atoms have a tetrahedral distribution, whereas complexes of bivalent copper and bivalent silver exhibit a planar configuration. An obvious extension of such investigations is to the stereochemistry of gold with its principal valencies of one and three. During the past few years various types of aurous and auric compounds, in which it was anticipated that the gold atom would be quadricovalent, have been examined by *X*-ray methods. The results have proved to be of unusual interest. Although the four valencies of the tervalent gold atom have been shown to lie in a plane with the metal, the univalent gold atom in the aurous compounds has been found to be bicovalent instead of quadricovalent, and the valency distribution probably linear. This apparent inability of aurous gold to attain a greater covalency than two has been discussed by Gibson (Presidential Address, Section B, British Association, 1938), who concludes that " there is no example of an aurous compound in which the gold atom is known to be 4-covalent, and attempts to produce such a compound have failed." Gibson considers that the substances $Et_3P(NH_3)_2AuCl$ and $(EtO)_3P(NH_3)_2AuCl$ prepared by Levi-Malvano (*Atti R. Accad. Lincei*, 1908, **17**, 857) may have a quadricovalent gold atom, as suggested by Mann and his co-workers, but Gibson gives reasons which indicate that this quadricovalency is by no means certain. There is, however, no doubt that aurous gold can be quadricovalent, for we have prepared a number of quadricovalent aurous complexes suitable for *X*-ray investigation by the use of 2 : 2′-dipyridyl and 4 : 5-(*o*-)phenanthroline as chelating groups in reactions with complex cyanides of the type $M^IAu(CN)_2$ where M^I = K, Tl, NH_4. The new derivatives are crystalline substances, $M^I[Au(CN)_2dipy]$ and $M^I[Au(CN)_2phenan]$. It might be suggested that in view of the tendency of gold to be bicovalent the compounds are really $[M^Idipy][Au(CN)_2]$ and $[M^Iphenan][Au(CN)_2]$. This idea cannot be maintained, however, for an *ammonium* derivative $NH_4[Au(CN)_2phenan]$ is readily isolated, and in this compound the nitrogen atom has already its maximum covalency of four, and the co-ordinating group must be associated with the gold atom. Again, by double decomposition of $K[Au(CN)_2phenan]$ with thallous nitrate, the *thallium* derivative $Tl[Au(CN)_2phenan]$ is readily obtained.

Although the isolation of these new derivatives is of definite theoretical interest, it is the stereochemistry of the quadricovalent aurous atom which has lent importance to this investigation. So far no exception has been found to the rule that when a quadricovalent metal atom has an effective atomic number identical with that of an inert gas its valency distribution is tetrahedral. In the new aurous complexes the effective atomic number of the gold atom is 86—that of radon—and it is reasonable to suppose, as various authors have already done, that the bond distribution would be tetrahedral. Actually the crystallographic evidence shows that the molecule of $K[Au(CN)_2dipy]$ has, in the solid state, a two-fold axis of symmetry. This is compatible both with a planar and with a tetrahedral distribution of valencies around the aurous gold, but the existence of a short axis (3·74 A.) completely eliminates the latter possibility. A double molecule of the type (I) is also excluded, because in such a molecule the dipyridyl residues would have to be at right angles to one another, or nearly so (in order to give a reasonable gold–gold separation), and this is clearly impossible with the short axis.



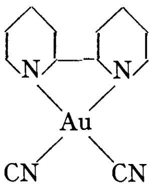
(I.)

$K[Au(CN)_2phenan]$ has a lower symmetry than the corresponding dipyridyl compound, but the existence of a short axis of exactly the same length (3·74 A.) indicates that the valency distribution cannot be tetrahedral, but is planar, or approximately so. A cursory examination of some of the intensities of the *X*-ray reflexions suggests also that the distribution of the molecules is similar to that in $K[Au(CN)_2dipy]$.

This unexpected finding that the bond distribution of the quadricovalent aurous atom is planar (or nearly so), like the quadricovalent auric atom, removes the last of the empirical rules which chemists have relied upon as a guide to the stereochemistry of quadricovalent atoms.

EXPERIMENTAL.

Potassium 2 : 2′-*Dipyridylaurocyanide*, $K[Au(CN)_2dipy]$.—This *compound* was prepared by adding 0·15 g. of 2 : 2′-dipyridyl, dissolved in 2 ml. of absolute ethyl alcohol, to 4 ml. of an aqueous potassium aurous cyanide solution, saturated at room temperature. On evaporation over phosphoric oxide in an evacuated desiccator, the salt crystallised as well-formed, colourless, orthorhombic needles (Found: Au, 44·6; C, 32·0; H, 1·8; N, 12·7. $C_{12}H_8N_4KAu$ requires Au, 44·4; C, 32·4; H, 1·8; N, 12·6%). The crystals show high birefringence ($>$ 0·20), the minimum refractive index being along the direction of elongation (*c*-axis). *X*-Ray measurements using Cu-K_α radiation show that the dimensions of the cell, which contains four molecules, are $a = 18{\cdot}15 \pm 0{\cdot}02$, $b = 18{\cdot}74 \pm 0{\cdot}02$, $c = 3{\cdot}74$ A. ($d_{obs.}$ 2·32, $d_{calc.}$ 2·31). The missing reflexions are $\{hkl\}$ absent for $h + l$ odd, and $\{0k0\}$ absent when k is odd. These halvings are characteristic of the space-group $B22_12 - D_2^5$, which requires eight general positions in the unit cell. Since, however, there are only four gold and four potassium atoms, these must lie on special positions, and consequently the molecule has an axis of symmetry. The molecule (II) can have only one such symmetry axis, which must pass through the gold atom and bisect the bond between the two pyridine rings. There are two sets of special positions in either of which the gold and potassium atoms may be located: (i) upon the *a*-axis, (ii) upon the *c*-axis. Since the length of the *c*-axis is 3·74 A., the gold atoms cannot be in the special positions (ii), because in that case the axis of symmetry of the molecule would have to be parallel to the *c*-axis. Consequently the co-ordinates of the gold atoms are $x, 0, 0;\ x, \tfrac{1}{2}, 0;\ x + \tfrac{1}{2}, 0, \tfrac{1}{2};\ \tfrac{1}{2} - x, \tfrac{1}{2}, \tfrac{1}{2}$. These are confirmed by the fact that, in general, all planes in the $\{hk0\}$ and $\{0kl\}$ zones with k odd are relatively weak. The potassium atoms cannot easily be located in the special positions (ii) because of lack of space, and their co-ordinates are probably $0, \tfrac{1}{4}, z;\ 0, \tfrac{3}{4}, \bar{z};\ \tfrac{1}{2}, \tfrac{1}{4}, z + \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{3}{4}, \tfrac{1}{2} - \bar{z}$, the atoms lying between four cyanide groups which are in a plane. The possibility of a tetrahedral distribution of valencies about the aurous gold can be completely eliminated by space-filling considerations. The short *c*-axis indicates that the dipyridyl residues lie in, or nearly in, the *c*-plane. The maximum tilt, allowing a carbon–carbon separation of 3·55 A., is 18°. Similarly it can be shown that the maximum tilt of the plane containing the gold atom and the two cyanide groups is *ca.* 25°, and consequently the maximum angle between this plane and the one containing the dipyridyl residues is *ca.* 43°. These deductions are obviously incompatible with a tetrahedral valency distribution, in which the angle would be 90°, and it is therefore necessary, in order to fit the molecules into the unit cell, to postulate a planar, or distorted planar, distribution of the valencies, the maximum distortion being defined by the above limits.



(II.)

The molecule as a whole has two degrees of freedom, rotation about the diad axis and translation along it. Space-filling considerations indicate that the translation is probably quite small, and also that the rotation of the dipyridyl residues is $\leqslant 18°$. The z co-ordinate of the potassium atom is probably approximately $\tfrac{1}{2}$, since in this position it is at a maximum distance from its nearest neighbours. It is noticeable that if the molecule is truly planar it has, in addition to the symmetry axis, a plane of symmetry, and also that if the molecule lies in the *c* plane the structure as a whole will also have a plane of symmetry parallel to the *b* axis, and symmetry centres at 0, ¼, 0; 0, ¾, 0; etc. A fairly strong pyroelectric effect, however, indicates that the crystal class is truly 222-D_2, and consequently that the molecule is tilted out of the *c* plane, thereby destroying the symmetry planes and centres. Whether the cyanide groups are tilted in the same direction as the dipyridyl or in the opposite direction to it, *i.e.*, whether the valency distribution is really planar or somewhat distorted, can only be determined by a detailed analysis of the structure, which we hope to carry out in the near future.

Potassium 4 : 5(*o*)-*Phenanthrolineaurocyanide*, K[Au(CN)$_2$phenan].—0·1 G. of 4 : 5-(*o*-)phenanthroline, dissolved in 1—2 ml. of absolute ethyl alcohol, was added to a solution of 0·4 g. of potassium aurous cyanide in 10 ml. of water. The *salt* separated at once as fine, colourless needles, insoluble in a large excess of cold water, but soluble on warming. The substance was recrystallised from absolute alcohol; it formed acicular monoclinic crystals, which were nearly all twins (Found: Au, 42·5; C, 36·2; N, 12·0. $C_{14}H_8N_4KAu$ requires Au, 42·1; C, 35·9; N, 12·0%). Addition of a concentrated thallous nitrate solution to a warm aqueous solution of the potassium salt affords the corresponding *thallous* salt, Tl[Au(CN)$_2$phenan], which is precipitated as colourless needles (Found: N, 8·8. $C_{14}H_8N_4TlAu$ requires N, 9·0%). The crystals of K[Au(CN)$_2$phenan] show high birefringence (> 0·20), the minimum refractive index being along the direction of elongation (*b* axis), and a fairly strong positive pyroelectric effect. The cell dimensions, determined from single-crystal rotation photographs, are $a = 41{\cdot}32 \pm 0{\cdot}05$, $b = 3{\cdot}74$, $c = 19{\cdot}82 \pm 0{\cdot}04$ A.; $\beta = 115^\circ\ 16'$. There are eight molecules in the unit cell ($d_{\text{obs.}}$ 2·22, $d_{\text{calc.}}$ 2·25). The missing reflexions are $\{hkl\}$ absent when $h + k$ is odd, and $\{h0l\}$ absent when *h* is odd and *l* is odd, characteristic of the space-groups *Cc* and *C*2/*c*. The positive pyroelectric effect eliminates *C*2/*c*, since this has a symmetry centre, and consequently the space-group is *Cc*. Although the above cell is the true one from the crystallographic point of view, the relation between the structure and that of K[Au(CN)$_2$dipy] can be seen more easily if it is referred to a body-centred cell having the following dimensions: $a = 37{\cdot}15 \pm 0{\cdot}04$, $b = 3{\cdot}74$, $c = 19{\cdot}82$ A.; $\beta = 92^\circ\ 14'$. The halvings are now $\{hkl\}$ absent when $h + k + l$ is odd, and $\{h0l\}$ absent when *h* is odd and *l* is odd. The cell dimensions are now comparable:

K[Au(CN)$_2$dipy].		K[Au(CN)$_2$phenan].	
a	18·74	*c*	19·82
b	18·15	*a*	18·57 × 2
c	3·74	*b*	3·74

The orders of $\{h00\}$ and $\{00l\}$ in the phenanthroline complex are very intense and are observed up to $h = 40$ and $l = 22$. $\{00l\}$ is halved, but $\{h00\}$ is quartered up to 1600, then 1800, 2200, 2600, etc., appear very weakly. All the $\{h0l\}$ reflexions for which *h* is even but not equal to 4*n* are also weak, therefore the cell dimensions are nearly $a = 18{\cdot}57$, $b = 3{\cdot}74$, $c = 19{\cdot}82$ A. These observations indicate that, although the K[Au(CN)$_2$phenan] crystal has lower symmetry than K[Au(CN)$_2$dipy], the distribution of the molecules within the unit cell, and the positions of the gold atoms, are similar. The existence of the short *b* axis also confirms the approximately planar arrangement of the gold valencies.

Ammonium 4 : 5-(o-)*Phenanthrolineaurocyanide*, NH_4[Au(CN)$_2$phenan].—A solution of ammonium cyanide containing approximately 2·5 g. in 100 ml. was prepared by double decomposition of solutions of ammonium sulphate and barium cyanide. 2 G. of aurous cyanide were added; 1·5 g. dissolved. The filtered solution containing ammonium aurocyanide was treated with 0·4 g. of *o*-phenanthroline dissolved in 3—4 ml. of absolute alcohol. The *salt* was precipitated immediately as colourless needles, which were recrystallised from alcohol (Found: Au, 44·3; C, 37·2; H, 2·6. $C_{14}H_{12}N_5Au$ requires Au, 44·0; C, 37·6; H, 2·7%). The unit cell of this compound has not been completely determined, but a short axis of 3·74 A. has been measured.

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