323. *The Stereochemistry of Quadricovalent Atoms: Cobalt and Manganese.*

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Stereochemical studies of the α- and the β-form of dipyridinocobaltous chloride have been made. Both these substances are monomolecular, and in the case of the α-chloride *X*-ray measurements show that the four groups linked covalently with the central cobalt atom have a *trans*-planar distribution, in striking contrast with the tetrahedral arrangement shown by Powell and Wells to occur in the $[CoCl_4]^{--}$ ion. Dipyridinomanganous chloride is found to be isomorphous with α-dipyridinocobaltous chloride; in this compound, therefore, the four covalencies of bivalent manganese also have a planar configuration.

β-Dipyridinocobaltous chloride is isomorphous with the only known forms of dipyridinocobaltous bromide and iodide; their stereochemistry is still uncertain.

From the stereochemical point of view, quadricovalent cobalt compounds present a problem of unusual interest. On the one hand, the ion $[CoCl_4]^{--}$ in Cs_3CoCl_5 has been shown by Powell and Wells (J., 1935, 359) to possess a tetrahedral configuration, and on the other hand the existence of two forms of diamminocobaltous chloride and similar substances, by analogy with the corresponding platinous compounds, has led to the suggestion (*e.g.*, by Biltz and Fetkenheuer, *Z. anorg. Chem.*, 1914, **89**, 97) that these substances are *cis*- and *trans*-isomerides of planar configuration. Sidgwick ("Electronic Theory of Valency," 1927, p. 230) has, however, pointed out that no certain conclusions as to the nature of the isomerism of the diammines of the cobaltous halides can be drawn from the available experimental evidence; nevertheless the possibility remained that bivalent cobalt might provide a definite example of a metal, in the same valency state, having both planar and tetrahedral quadricovalent derivatives.

In order to test this possibility we have made a new study, by chemical and crystallographic methods, of the two forms of dipyridinocobaltous chloride, $CoCl_2 2py$, and some related compounds. The violet α-form, which is stable at room temperature, was prepared in 1894 by Reitzenstein (*Annalen*, **282**, 267); the blue β-form was obtained by Hantzsch and Schlegel (*Z. anorg. Chem.*, 1927, **159**, 273), who dissolved the violet form in boiling chloroform and precipitated the β-chloride by addition of ligroin. This β-form is also obtained when the α-form is heated for a few hours in a sealed tube at 110—120°. Hantzsch and Schlegel prepared a blue bromide and a green iodide of analogous composition, which have so far been obtained in one form only. All these substances give red solutions in water, indicating decomposition. When the chloride $CoCl_2 2py$ is dissolved in acetone, alcohol or chloroform, a deep blue solution is obtained, and this, on evaporation at room temperature, deposits crystals of the α-form, independent of which form was originally dissolved. If, however, the evaporation takes place at a higher temperature, the β-form is produced. The same phenomena are observed when ligroin is added to a chloroform solution, *i.e.*, cold solutions yield the α- and hot solutions the β-form.

We have determined the molecular weights of the two forms by the cryoscopic method in phenol and by the ebullioscopic method in chloroform, obtaining results which indicate in both cases the simple formula $CoCl_2 2py$. The results in boiling chloroform fully establish the monomeric character of the β-form, which is the stable modification under the experimental conditions; since cobaltous chloride is insoluble in chloroform, any dissociation would readily be detected. The evidence of the molecular weights is not so valuable in the case of the α-form, on account of its possible transformation into the β-isomeride; our *X*-ray measurements on the crystalline α-modification, however, show clearly not only that it is monomeric, but also that it possesses a planar *trans*-configuration. This conclusion is based chiefly on the observation that the minimum distance between cobalt atoms in neighbouring molecules is 3·65 A.; so short a distance is only possible with molecules that are almost completely flat and therefore have their pyridine groups in *trans*-positions (cf. the case of the corresponding copper compound; Cox, Sharratt, Wardlaw, and Webster, J., 1936, 129). It has already been pointed out (Barkworth and Sugden, *Nature*, 1937, **139**, 374) that the assumption of the structure $[CoCl_4][Co4py]$ for the violet form leads to difficulties in the interpretation of the magnetism of cobalt complexes; this structure, and the other possible dimeric formula $[CoCl_3py][CoCl3py]$, are directly excluded by the *X*-ray data, since, as reference to models shows, neither the $[Co4py]^{++}$ nor the $[CoCl3py]^+$ ion could be sufficiently flat, on account of the mutual obstruction of the pyridine rings. Apart from this consideration, the short Co. . .Co distance with the dimeric formulæ would necessitate a most improbable structure in which ions of the same sign were in contact throughout the crystal.

The crystallographic evidence does not lead to any definite conclusion regarding the structure of the β-form, but it does show that it is isomorphous (and therefore, presumably, isostructural) with the only known forms of dipyridinocobaltous bromide and iodide. The interconversion of the α- and β-modifications with change of temperature and the fact that they are now both shown to be monomolecular suggest that they may be dimorphous forms of one compound having a planar *trans*-structure, but against this view are the pronounced differences in colour and magnetism; it remains a possibility that the β-form has a *cis*-planar or tetrahedral configuration.

The demonstration of the planar structure of α-dipyridinocobaltous chloride together with the previouslyestablished tetrahedral structure of the $[CoCl_4]^{--}$ ion (Powell and Wells, *loc. cit.*) appears to constitute the first definite case of a bivalent metal possessing simple unchelated quadricovalent derivatives of more than one configuration; this is in marked contrast with the stability of configuration among the metals of the platinum group, where considerable changes in the nature of the addenda and in the state of ionisation of the complex as a whole have no effect on the planar distribution of the four metal valencies. In the case of bivalent platinum in particular, the planar distribution of the bonds in many quadricovalent compounds has been demonstrated so completely both by chemical and by physical methods that there seems little room for doubt that no other configuration is possible. Whether the different behaviour of cobalt is to be attributed to possible alternative electron distributions, to the nature of the links (co-ordinate or homopolar, etc.), or to other causes is a matter for further investigation.

We have also studied dipyridinomanganous chloride, $MnCl_22py$, and find that it possesses a planar *trans*-structure, being fully isomorphous with α-dipyridinocobaltous chloride. [It is of interest that the corresponding copper compound (Cox, Sharratt, Wardlaw, and Webster, *loc. cit.*), while remarkably similar in structure to the cobalt and manganese derivatives, is not isomorphous with them.] Apart from the phthalocyanin derivative (Linstead and Robertson, J., 1936, 1736) with its somewhat exceptional character, this appears to be the first demonstration of the configuration of a simple quadricovalent derivative of bivalent manganese. The result emphasises an aspect of the stereochemistry of the metals which we have previously pointed out, *viz.*, the dependence of configuration on principal valency, since, as is well known, both $[MnO_4]'$ and $[MnO_4]''$ are tetrahedral.

EXPERIMENTAL.

α-*Dipyridinocobaltous Chloride.*—Cobaltous chloride hexahydrate (26 g.) was triturated with pyridine (16 g.), and the mixture extracted with hot alcohol. On cooling, pale mauve crystals separated, which were recrystallised from alcohol, washed with alcohol and ether, and dried over phosphoric oxide in a vacuum (Found : Co, 20·7; Cl, 24·5; N, 10·1. Calc. for $CoCl_2,2C_5H_5N$: Co, 20·5; Cl, 24·6; N, 9·7%).

Cryoscopic determination in phenol (constant = 7·27° per 1000 g.). 30·32 G. per 1000 g. gave $\Delta t = 0·863°$, whence $M = 255$. 38·82 G. per 1000 g. gave $\Delta t = 1·143°$, whence $M = 247$.

Ebullioscopic determination in chloroform (constant = 26° per 100 ml.). 17·84 G. per 1000 ml. gave $\Delta t = 0·136°$, whence $M = 341$. 19·19 G. per 1000 ml. gave $\Delta t = 0·141°$, whence $M = 354$ (Calc. for $CoCl_2,2C_5H_5N$: M, 288).

β-*Dipyridinocobaltous Chloride.*—The α-form was heated in a sealed tube for a few hours. The tube was opened while still hot, and the contents transferred to a cool beaker in the absence of moisture. A blue powder was obtained (Found : Co, 20·7; Cl, 24·6%). A second method of preparation consists in dissolving the α-form in chloroform and adding ligroin to the boiling solution; a blue powder is at once precipitated; this is washed with ether and dried as above (Found : Co, 20·7%).

To obtain the β-form as *crystals*, a chloroform solution of the α-form is evaporated to dryness on the water-bath. The blue crystals are removed and dried as above (Found : Co, 20·3%).

Cryoscopic determination in phenol. 32·83 G. per 1000 g. gave $\Delta t = 0·887°$, whence $M = 269$. 59·33 G. per 1000 g. gave $\Delta t = 1·521°$, whence $M = 284$.

Ebullioscopic determination in chloroform. 13·31 G. per 1000 ml. gave $\Delta t = 0·111°$, whence $M = 312$. 12·85 G. per 1000 ml. gave $\Delta t = 0·108°$, whence $M = 309$.

β-*Dipyridinocobaltous Bromide.*—Hydrated cobalt bromide (20 g.) was dissolved in boiling alcohol, and pyridine (10 g.) added. Small blue crystals were obtained, recrystallisable from alcohol or chloroform (Found for a sample recrystallised from the latter solvent and dried over phosphoric oxide : Co, 15·7; Br, 42·3. Calc. for $CoBr_2,2C_5H_5N$: Co, 15·6; Br, 42·5%).

β-*Dipyridinocobaltous Iodide.*—Cobalt carbonate was dissolved in hydriodic acid, the solution evaporated to dryness, and the product recrystallised from alcohol. 20 G. of this cobaltous iodide were dissolved in boiling alcohol and treated with pyridine (10 g.). Small green crystals were obtained, which were washed with alcohol and ether and dried as before (Found : Co, 12·6; I, 53·9. Calc. for $CoI_2,2C_5H_5N$: Co, 12·5; I, 53·9%).

Dipyridinocobaltous Oxalate.—Hydrated cobalt chloride (2·4 g.) was dissolved in hot pyridine and added to a solution of oxalic acid (1·3 g.) in pyridine. A red powder was at once precipitated; this was filtered off, washed, and dried over calcium chloride (Found : Co, 19·2. $CoC_2O_4,2C_5H_5N$ requires Co, 19·3%).

It has also been found possible to obtain the β-form of dipyridinocobaltous chloride by a method described by Reitzenstein for the preparation of the compound $CoCl_22py,2C_2H_5{\cdot}OH$. If tetrapyridinocobaltous chloride is dissolved in alcohol, a blue compound crystallises. This substance, which rapidly reverts to a violet stable compound, was supposed by Reitzenstein to be the above alcoholate (no analyses were obtained), and the violet compound the α-form of dipyridinocobaltous chloride. We have confirmed the latter observation, but find that the blue substance (which we have isolated) is not the alcoholate, but β-dipyridinocobaltous chloride (Found : Co, 20·5%).

Crystallographic Results.—*X*-Ray measurements were made by means of single-crystal rotation and oscillation photographs with copper Kα radiation.

α-Dipyridinocobaltous chloride occurs as thin needles, strongly dichroic, and showing nearly straight extinction. The crystals are monoclinic, the forms observed in the needle zone being *a*{100} and *m*{110} (*a* : *m* = 62° approx.). The cell dimensions are *a* = 17·2, *b* = 34·1, and *c* = 3·65 A.; β ≈ 90°. The unit cell is *c*-face-centred and contains eight molecules of $CoCl_2 2py$ (*d* calc. = 1·81 g./c.c.; obs., 1·76). The space-group was not determined.

Apart from the small difference in the lengths of the axes, the *c*-axis rotation photograph of this substance is scarcely distinguishable from the corresponding one of dipyridinocuprous chloride (*b* = 8·4, *a* = 34·0, *c* = 3·84 A.), so that from these photographs alone it might be inferred that the two are isomorphous; measurement of the other axes, however, shows that this is not the case, although there is clearly a very close relation between the two structures.

β-Dipyridinocobaltous chloride forms well-developed, six-sided, columnar crystals, originally deep blue, which break down to a pale blue powder after a few hours' exposure to the atmosphere. They appear to be orthorhombic combinations of a prism *m* with a pinacoid *a* (*a* : *m* = 65° approx.), the length of the prism axis being *c* = 8·30 A. This is a symmetry axis and appears to be the shortest cell dimension.

Dipyridinocobaltous bromide and iodide occur in imperfectly formed, six-sided, columnar crystals with *a* : *m* = 65° and 63°, and *c* = 8·42 and 8·68 A. respectively. Comparison of the interfacial angles and the rotation photographs leaves no doubt that the bromide and iodide are isomorphous with the β-chloride, differing materially from the α-chloride. Owing to the deliquescence of these substances, more detailed examination could not be carried out.

Dipyridinomanganous chloride forms pale rose-pink, deliquescent needles, which, apart from colour, are similar in all respects to the crystals of α-dipyridinocobaltous chloride. The close correspondence of the *X*-ray photographs and of the angles in the *c*-zone (*a* : *m* = 59° approx.) shows beyond doubt that the two substances are isomorphous. The length of the *c*-axis is 3·73 A.; on account of their deliquescence crystals could not be preserved long enough to measure the other axes accurately, but these are approximately the same as the corresponding axes in the cobalt compound (*a* = 17, *b* = 34 A.).

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