# Crystal-Chemical Data on the Stereochemistry of Complex Compounds of Certain Divalent Transition Metals (Fe, Co, Ni, Cu, Pd, and Pt)

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## Abstract

## Full Text

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# Crystal-Chemical Data on the Stereochemistry of Complex Compounds of Certain Divalent Transition Metals (Fe, Co, Ni, Cu, Pd, and Pt)

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In recent years, more than 30 X-ray structural studies of complex compounds of divalent Co, Ni, Pd, and Pt have been carried out in the crystallochemistry laboratories of the Institute of General and Inorganic Chemistry and Moscow State University. These results (1–22), together with other data, make it possible to establish certain characteristic features in the stereochemistry of complex compounds of metals in the horizontal series Fe, Co, Ni, Cu and the vertical series Ni, Pd, Pt.*

Table 1 presents statistical data on the coordination polyhedra of Fe, Co, Ni, Cu, Pd, and Pt atoms according to the available structural data (only complex compounds are included, comprising hexaammine complexes and hexahydrates, dimeric complexes, chain structures of the type $MA_2X_2$, and inner-complex compounds; compounds of the type of double oxides and sulfides and other oxygen compounds have not been taken into consideration). Table 2 gives a general picture of changes in coordination and magnetic state upon replacement of addends in the series CN, $NO_2$, NCS, Br, Cl, O, F, corresponding to a gradual increase in bond polarity, and upon replacement of an acidic addend by a neutral substituent.

In analyzing the structural data, other physicochemical properties (chemical, magnetic, dielectric, and spectral), essential for establishing analogies in the structure of individual classes of compounds, were naturally also taken into account.

**Table 1**

Statistical data on coordination polyhedra in complex compounds of divalent Fe, Co, Ni, Cu, Pd, and Pt

| Coordination polyhedron | Fe | Co | Ni | Cu | Pd | Pt |
|---|---|---|---|---|---|---|
| Square | | 1 | 19 | 6 | 19 | 29 |
| Tetrahedron | | 11 | 1 | 1 | | |
| Octahedron | 34 | 30 | 51 | 9 | | |
| Elongated square bipyramid | | | | 22 | ? | ? |

| Coordination polyhedron | Fe | Co | Ni | Cu | Pd | Pt |
|---|---|---|---|---|---|---|
| Flattened square bipyramid | | | | 3 | | |
| Square pyramid | | | | 2 | | |
| Total number of structures studied | 34 | 42 | 71 | 43 | 19 | 29 |

1. As is well known, compounds of divalent Pd and Pt are invariably diamagnetic and are characterized by a planar structure of the complexes, irrespective of their composition. Structural studies have shown that square coordination is preserved in complete "purity" also in crystalline— in the crystalline state. The only exceptions are $M(\text{diarsine})_2J_2$ ($M = \text{Ni, Pd, Pt}$) (25), $[\text{Pt}(\text{NH}_3)_4(\text{NCCH}_3)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (26), $M^{II}(\text{NH}_3)_2\Gamma_2 \cdot M^{IV}(\text{NH}_3)_2\Gamma_4$ ($M = \text{Pd, Pt}$; $\Gamma = \text{Cl, Br}$) (27,28), in which the squares $M\text{As}_4$, $\text{Pt}(\text{NH}_3)_4$, and $M(\text{NH}_3)_2\Gamma_2$ are supplemented to distorted octahedra by pairs of addends situated at large distances from $M$ (3-3.5 Å). However, the interpretation of these complexes as $M(\text{ad}')_4(\text{ad}'')_2$ on the basis of $dsp^3d$ (or, in other words, $dsp^2 + p_{zd_z^2}$) hybridization of covalent bonds (25) appears very questionable. It seems more probable that between $M$ and the two remote addends ad″ there is only electrostatic interaction. This is confirmed by the fact that the distances between ad″ and ad′ correspond to sums of ionic or intermolecular radii.

2. In contrast to Pt and Pd, nickel gives diamagnetic compounds with a square configuration of the complexes only with addends forming the most covalent bonds: in the acido series, only with CN groups; among ordinary complex compounds of composition $\text{NiA}_2\text{X}_2$, only with certain phosphines. Among inner-complex compounds, planar coordination is much more widespread. Such a structure is possessed in almost all cases by the units $\text{NiN}_4$, $\text{NiS}_4$, $\text{NiN}_2\text{S}_2$, and in many cases also by $\text{NiN}_2\text{O}_2$ and $\text{NiS}_2\text{O}_2$ (29). The latter, as well as $\text{Ni}(\text{PR}_3)_2\text{X}_2$, lie on the boundary separating dia- and paramagnetic complexes; the structure here depends on relatively secondary factors (on the groupings in which the atoms N, S, or P participate).

The remaining Ni complex compounds, as a rule, are paramagnetic and have octahedral coordination. The only exceptions are $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}_2$ (and possibly $[(\text{C}_6\text{H}_5)_3\text{CH}_3\text{As}]_2 \cdot \text{NiCl}_4$), to which the authors (30,31) ascribe a tetrahedral structure. The latter may be explained by the fact that the presence of such bulky addends as $\text{P}(\text{C}_6\text{H}_5)_3$ or cations $(\text{C}_6\text{H}_5)_3\text{CH}_3\text{As}^+$ creates steric hindrance to the formation of polymeric chains or frameworks characteristic of other halogen-containing nickel compounds (for example, $\text{CsNiCl}_3$, $\text{NiA}_2\text{Cl}_2$,

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* For other elements of group eight—Rh, Ir, and Os—the divalent state is not characteristic, and in the case of Ru only two structures have been studied: $K_4[Ru(CN)_6] \cdot 3H_2O$, isomorphous with the analogous ferrocyanide (23), and $M^I RuFe^{III}(CN)_6$, where $M^I$ is an alkali metal (24).

where $A = H_2O$, Py ([32,13])). In general, tetrahedral coordination is not characteristic of ordinary complex compounds of Ni (for details see ([33])).

3. The stereochemistry of Co$^{II}$ compounds differs substantially from that of Ni$^{II}$. In the series of acido complexes, the transition from low-spin to high-spin compounds

**Table 2**

**Dependence of the coordination of the metal atom on the composition of the complex**

| Element | CN | $NO_2$ | NCS | Br | Cl | F | O | Spinels | $MeA_2X_2$ | $MeA_4X_2$ | $MeA_6X_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | Octahedron (low-spin) | Octahedron (low-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Tetrahedron with all $M^{III}$, except Fe$^{III}$ | Octahedron | Octahedron | Octahedron |
| Co | Octahedron (low-spin) | Octahedron (low-spin) | Tetrahedron (high-spin) | Tetrahedron (high-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Octahedron (high-spin) | Octahedron with Fe$^{III}$, tetrahedron with Cr$^{III}$, Mn$^{III}$, Co$^{III}$ | Tetrahedron, octahedron (two isomers) | Octahedron | Octahedron |
| Ni | Square (low-spin) | Octahedron (high-spin)* | Octahedron (high-spin)* | Octahedron (high-spin)* | Octahedron (high-spin)* | Octahedron (high-spin)* | Octahedron (high-spin)* | Octahedron with all $M^{III}$, except Cr$^{III}$ | Square, octahedron** | Octahedron | Octahedron |

| Element | CN | $NO_2$ | NCS | Br | Cl | F | O | Spinels | $MeA_2X_2$ | $MeA_4X_2$ | $MeA_6X_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | Octahedron | Flattened tetrahedron | Flattened tetrahedron | Distorted octahedron | Distorted octahedron | Distorted octahedron | Distorted octahedron | Distorted octahedron with all $M^{III}$, except $Cr^{III}$, $Mn^{III}$ | Square, distorted octahedron, pyramid | Square, distorted octahedron | Distorted octahedron |
| Pd, Pt | Square (low-spin) | Square (low-spin) | Square (low-spin) | Square (low-spin) | Square (low-spin) | Square (low-spin) | Square (low-spin) | – | Square | Square | – |

* Possibly with the exception of $[As(C_6H_5)_3CH_3]_2NiCl_4$.

** With the exception of $Ni[P(C_6H_5)_3]_2Cl_2$ (tetrahedron).

occurs later—after the $NO_2$ groups; moreover, for low-spin compounds the characteristic coordination of M is not planar but octahedral, whereas for high-spin compounds—in the case of NCS, Br, and Cl—it is not octahedral but tetrahedral. Only on passing to the most electronegative addends, F and O, does the coordination of Co^II and Ni^II become the same—octahedral*. The transition from tetrahedral to octahedral complexes is promoted not only by an increase in the polarity of the Co–X bond, but also by replacement of acidic addends by neutral ones such as $H_2O$, $NH_3$, Py, thio, and others. Thus, compounds of composition $CoA_2X_2$ (where X = NCS, Br, Cl) have two modifications, in one of which tetrahedral coordination is retained, while in the other octahedral coordination is created (a chain polymeric structure); compounds $CoA_4X_2$, and still more so $CoA_6X_2$, are always built of octahedral complexes.

In its ability to form tetrahedral complexes, Co occupies a special position among the divalent transition metals of groups 8 and 1b.

4. Structural data on complex compounds of divalent iron are very limited. The available material seems to show that only octahedral coordination is characteristic of F^II in complex compounds. Consequently, in low-spin compounds (cyano and nitro) Fe^II exhibits an analogy with Co^II, and in high-spin compounds—with Ni^II*.
5. Divalent copper, stereochemically, occupies an intermediate position, on the one hand between Ni^II and Pd^II, Pt^II, and on the other hand between Ni^II and Co^II. Like Pd and Pt, copper sometimes gives purely planar complexes, as well as planar complexes supplemented by an M–

M bond. However, the coordination most characteristic of Cu^II is in the form of an elongated bipyramid. The filling of all five levels of the 3d shell of the Cu^II atom by nine electrons makes it possible to compare such Cu complexes both with spin-paired square complexes of Pt, Pd, and Ni and with spin-free octahedral complexes of Ni. The similarity to planar complexes is emphasized by the fact that the Cu—ad′ distances (to as many as four addends arranged in a square) are close to the M—ad distances (M = Pt, Pd, Ni) in square complexes and are smaller than Ni—ad in octahedral ones; the similarity to octahedral complexes is shown by the structural closeness of many Cu compounds and paramagnetic Ni compounds (for example, $CuF_2$ and $NiF_2$, $CuCl_2$, $CuBr_2$ and $NiCl_2$, $NiBr_2$, $CsCuCl_3$ and $CsNiCl_3$, $K_2Pb[Cu(NO_2)_6]$ and $K_2Pb[Ni(NO_2)_6]$, $Cu(NH_3)_4(NO_2)_2$ and $Ni(NH_3)_4(NO_2)_2$, etc.). In all the cases listed, the structural motif of the Cu compound may be represented as a distortion of the structure of the analogous Ni compound. The presence of one vacant place in the d shell of the Cu^II atom is associated also with copper' s tendency toward other distorted or low-symmetry coordinations: toward an unevenly elongated octahedron, toward a tetragonal-pyramidal environment, and toward the affine isomer of a tetragonal-bipyramidal complex—a "flattened" octahedron (34).

On the other hand, in the series of copper halides a transition is observed from structures characteristic of Ni^II to structures characteristic of Co^II: $CuCl_2$ and $CsCuCl_3$ are isostructural (with distortion) with the analogous Ni compounds; $Cs_2CuCl_4$ is isomorphous with $Cs_2CoCl_4$. Distorted-tetrahedral coordination may also be expected in copper rhodanide compounds (for example, in $Cu(NCS)_4Hg$, whose composition is analogous to the corresponding double salt of Co and Hg, but not of Ni and Hg).

6. Many of the compounds of the divalent metals considered are isomorphous. Isostructurality is manifested in two groups of compounds: 1) among the low-spin compounds of the vertical series Pt, Pd, Ni, where it is determined by the creation of hybrid covalent bonds on the basis of analogical electronic systems*; 2) among the most ionic high-spin compounds of the horizontal series—Fe, Co, Ni (and Cu, with distortion of the coordination polyhedron), where the crystal structure is determined by the stabilizing influence of the electrostatic field of the addends, in all cases (independently of the number of electrons at the central atom) octahedral coordination is more favorable than tetrahedral. In the intermediate region—on going from the most electronegative addends F and O to Cl, Br, and NCS—the structure of the complex is deter-

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* Exceptions are oxygen compounds of the spinel type—M^II $M_2$^III $O_4$, where Fe^II and Co^II much more often than Ni^II and Cu^II are displaced into tetrahedral voids by atoms of a trivalent metal (35, 36). Tetrahedral coordination of Co^II has also been found in $BaCoO_2$, and of Fe^II in some sulfides.

mined by the superposition of both effects. Calculations for oxides and hydrates show that the excess of the stabilizing strength of the octahedral field over the tetrahedral one decreases in the series Ni, Cu, Fe, Co (35, 36) (according to (36) this excess is equal to 22.8; 15.6; 2.9; 2.1 kcal, respectively). It is therefore natural that Ni^II is least inclined to change octahedral coordination to another type, and Co^II to the greatest extent. On the other hand, the very ability to form tetrahedral covalent bonds is apparently connected with symmetrical filling by electrons of the energy levels of the *d*-shell that do not participate in the bonds. Therefore such bonds are formed in Co^II compounds (configuration $d^7 = d_\gamma^4 d_\varepsilon^3$), and much more rarely in Fe^II compounds (configuration $d^6 = d_\gamma^3 d_\varepsilon^3$ with asymmetric filling of the $d_\gamma$ doublet).

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* In individual cases (chiefly in inner-complex compounds with organic addends sufficiently "rigid" in structure), low-spin Ni^II compounds are isomorphous with Cu^II compounds despite the presence of an extra electron at the Cu atom.

*Note: Figure translations are in progress. See original paper for figures.*

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