

Stereochemical aspects of macrocyclic polyphosphanes and polyarsanes and of their metal complexes

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Abstract — Polyphospha- and polyarsa-macrocycles may occur as diastereoisomeric forms which are stable at room temperature. The ligational behaviour of four series of potentially six-dentate tetraphospha- diheteramacrocycles is discussed. Some of the five possible diastereoisomers of each series actually act as six-dentate ligands but others can bind only as five- or four-dentate. The role of the ring size as well as of the nature of both the heteroatom and the metal ion is examined.

In contrast to the intense interest which has been devoted to synthetic polyheteramacrocycles containing oxygen, nitrogen, or sulfur since the 1960s, the attention paid to polyphospha- or polyarsa-containing macrocycles as potential ligand is quite recent. Synthetic troubles and the lack of biological relevance may account for this delay. As a matter of fact, the first metal complex containing a coordinated phosphano group of a macrocycle has been described as late as in 1974.¹ Since then the field is in the process of such rapid expansion that now about sixty macrocyclic phosphanes, either as free ligands or as their metal complexes obtained by template reactions, and about twenty macrocyclic arsanes are known.² These figures do not take into account the occurrence of their stable diastereoisomers for polyphosphanes or polyarsanes. Actually, tertiary phosphanes and arsanes have barriers to inversion at P and As in excess of 30 and 40 kcal/mol, respectively.³ The above macrocycles, therefore, can exist at room temperature in a number of stable diastereoisomers which, in principle, may be isolated or, more often, detected by nmr spectroscopy (³¹P, ¹H, and ¹³C). Whenever single isomers are heated according to proper temperature-time conditions, interconversion among various diastereoisomers can often be achieved and eventually the equilibrium mixture can result.

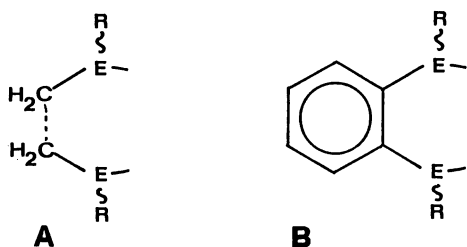


Fig. 1. A and B subunits of macrocycles; E=P or As

In considering the stereochemical features arising from the relative chirality of the phosphano or arsano groups for these macrocycles, the two kinds of subunits A and B should be distinguished (Figure 1).¹ With the four saturated |18|ane- or |22|ane-tetraphosphadiheteramacrocycles L¹ (Figure 2)¹ which contain only A moieties, all of the five possible diastereoisomers L¹ to L⁵, resulting from the four chiral phosphorus atoms, occur in nearly statistical amounts in the reaction mixture or upon thermal equilibration.⁴⁻⁷

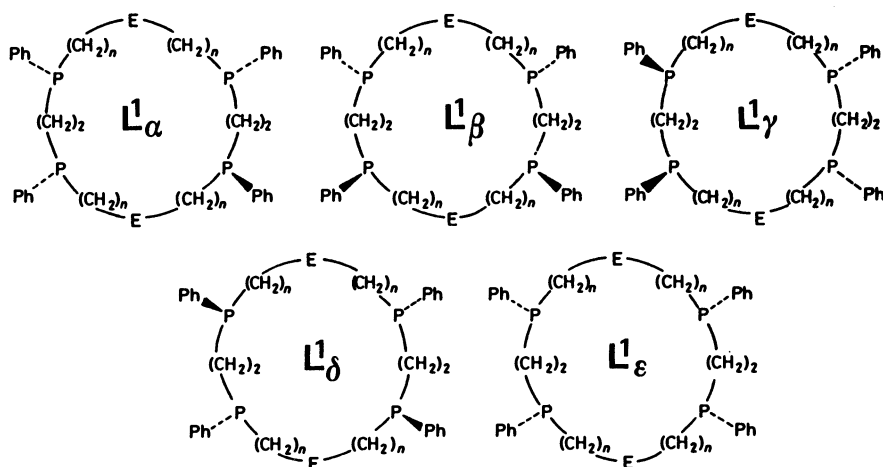


Fig. 2 The five diastereoisomers of L^1 ; $n=2$, $E=O$, $L^1=P_4O_2$; $E=NPr$, $L^1=P_4N_2$; $E=S$, $L^1=P_4S_2$. $n=3$, $E=S$, $L^1=|22|P_4S_2$

This suggests that both internal and solvation energy terms are nearly the same for each isomer. With both P_4O_2 and P_4S_2 , all of the five diastereoisomers have been isolated whereas only four and three of them were respectively obtained with P_4N_2 and $|22|P_4S_2$. With other A-type macrocycles containing phosphano or arsano groups, the existence of a number of diastereoisomers has been ascertained but, so far, the single isomers have seldom been identified.^{8,9}

The *o*-bis(alkylphenylphosphano)benzene moiety, B ($E = P$, $R = Ph$), always exhibits a *cis*-configuration of the two phenyl groups in all of the fifteen known examples.¹⁰⁻¹³ Conversely, with the *o*-bis(alkylmethylarsano)benzene subunits, B ($E = As$, $R = Me$), both the *cis*- and *trans*-configurations of the methyl groups has often been found.¹³ It must be stressed that the non-occurrence of the *trans*-(PhP)₂ species is probably thermodynamic (enthalpic) and not kinetic in origin since thermal equilibration experiments do not result into formation of the *trans*-species to any detectable amount.¹⁰⁻¹³

Whenever a B moiety is connected to another B one or to a phosphano or arsano group by aliphatic chains, the pair of chiral atoms at the end of the chain exhibit either the same or the opposite configuration. The equilibrium amounts of the stereoisomeric forms may significantly differ from the statistical ratio for the various compounds.¹⁰⁻¹³ Rather subtle conformational and solvation effects must be operative, in these cases, which make the various diastereoisomers energetically different among themselves.

The various diastereoisomers often exhibit different ligational capabilities such as different denticity of the macrocycle and different stereochemistry of their coordination compounds. Actually, the occurrence of chiral sites in annular ligands often prevents some of the potential donors from being located in a proper stereochemical position for a convenient coordination to the metal.

A simple example is given by the following macrocycles L^2 (Figure 3).¹² Since the cavities of these macrocycles are too small to enclose a transition metal, only the *fac*-tridentate bonding arrangement may at most result. As a matter of fact, the *meso-cis*-stereoisomers act as tridentate ligands giving, e.g., *fac*-octahedral $Mo(CO)_3(L^2)$ complexes. Conversely, the *meso-trans*-stereoisomers have their E' atom sterically ineffective to *fac*-coordination, once the two E donors have bound the metal. Thus, they act in a bidentate fashion, the E' atom being uncoordinated in the $Mo(CO)_4(L^2)$ compounds.

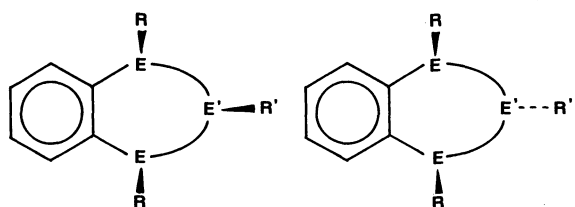


Fig. 3.
Potentially tridentate L^2 macrocycles:
 $E=E'=P$ or As ; $R=Me, Ph$; $R'=Ph$.

A broader variety of ligational behaviour occurs with the potentially six-dentate L^1 macrocycles whose stereochemistry of the complexes with iron(II), cobalt(II), and nickel(II) strongly depends on the relative chiralities of the phosphorus atoms, although additional factors must also be considered such as the donor strength of E, the ring size, and the nature the metal ion. The four phosphano groups always coordinate the metal ion but the remaining O, S, or N donors may or may not coordinate it.

When the four phosphorus atoms adopt a planar coordination arrangement, a heteroatom can reach an axial coordination position either with a facial or with a meridional arrangement of the $(Ph)P...E...P(Ph)$ moiety. In the former case, both phenyl groups must be on the same side of the plane of the free macrocycle, namely the two phosphane groups have opposite chirality (Figure 4, a). Conversely, if a meridional arrangement occurs, both phenyl groups must be on opposite sides of the macrocycle plane, the two phosphane groups having the same chirality (Figure 4, b). It must be noticed, however, that the two $P...E...P$ moieties of the macrocycle are not completely independent from each other but, owing to the annular hindrance, they mutually interfere upon metal wrapping.

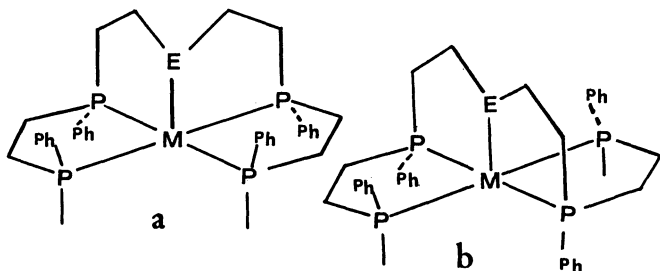


Fig. 4.
Two possible arrangements of the $P...E...P$ subunits with a square-planar P_4 coordination.

This situation holds true for P_4O_2 . The ether oxygen is a weak and rather hard donor as compared with phosphano groups towards transition metal ions. The four phosphorus atoms do surround the metal ion in a square-planar fashion thus creating a strong in-plane field. With the β - and δ -isomers, all-facial⁴ and all-meridional¹⁴ (Figure 5) coordination of the two $P...O...P$ moieties can respectively occur without mutual interference, so the six-coordination of the metal may result.

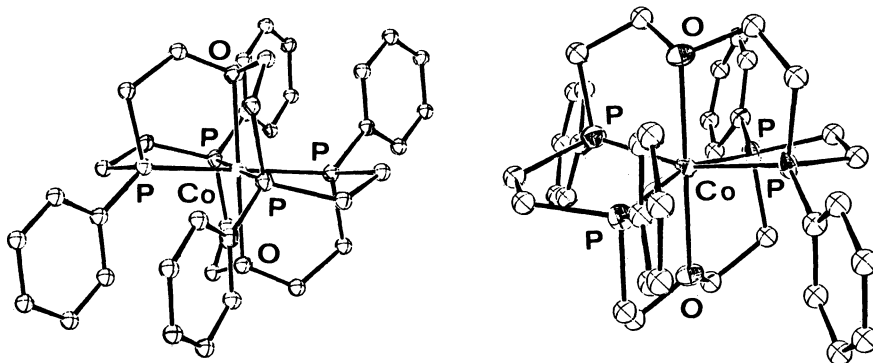


Fig. 5. ORTEP views of the cations $|Co(\beta-P_4O_2)|^{2+}$ (left) and $|Co(\delta-P_4O_2)|^{2+}$ (right).

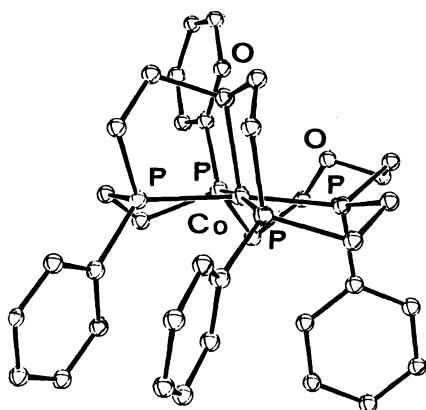


Fig. 6. A view of $|\text{Co}(\alpha\text{-P}_4\text{O}_2)|^{2+}$.

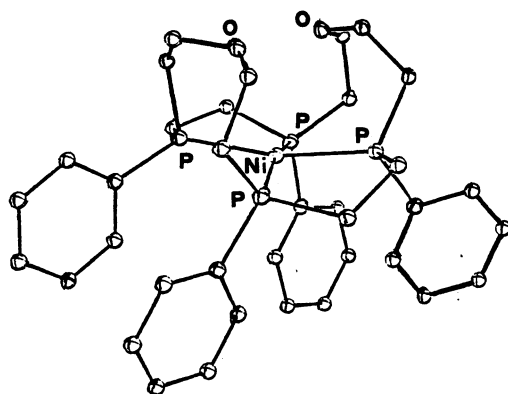


Fig. 7. A view of $|\text{Ni}(\epsilon\text{-P}_4\text{O}_2)|^{2+}$

Conversely, with the α -isomer⁴, one P...O...P chain links phosphorus atoms of opposite chirality whereas the other chain links phosphorus atoms of the same chirality. This isomer behaves as a five-dentate ligand toward cobalt(II) (Figure 6) only facial coordination of the P(RS)...O...P(SR) moiety taking place. In fact, molecular models show existence of mutual interferences between the two P...O...P moieties, so that neither fac-/mer-octahedral nor mer-square-pyramidal coordination can occur with a planar arrangement of phosphorus atoms.¹⁵

The ϵ -isomer has both P...O...P moieties available for tridentate facial coordination. Nonetheless, the two moieties are linked by ethylenic chains in a syn arrangement so that both ether oxygens do compete with each other for the same apical position of a square pyramid. Such an isomer, therefore, is expected to act as a five-dentate ligand or as a ligand forming two very weak M-O interactions from the same side of a square-planar complex. Actually, the X-ray crystal structure determination of the $|\text{Ni}(\epsilon\text{-P}_4\text{O}_2)|^{2+}$ ion (Figure 7) has shown that the two ethereal oxygen atoms lie on the same side of the NiP₄ average plane with slightly different Ni-O distances, ranging between 2.97 and 3.22 Å.¹⁶ These figures are definitely non-bonding ones.

Finally, the γ -isomer does not allow the facial coordination of P...O...P moieties whereas the meridional coordination is an incompatible one with a P₄ planar arrangement, due to internal hindrance. Indeed, this isomer acts as a four-dentate ligand in its cobalt and nickel complexes.¹⁷ The same denticity is also shown by $\gamma\text{-P}_4\text{N}_2$, which gives square-planar nickel complexes and square-pyramidal cobalt⁴ ones by further addition of a water molecule or a halide ion (Figure 8).⁶

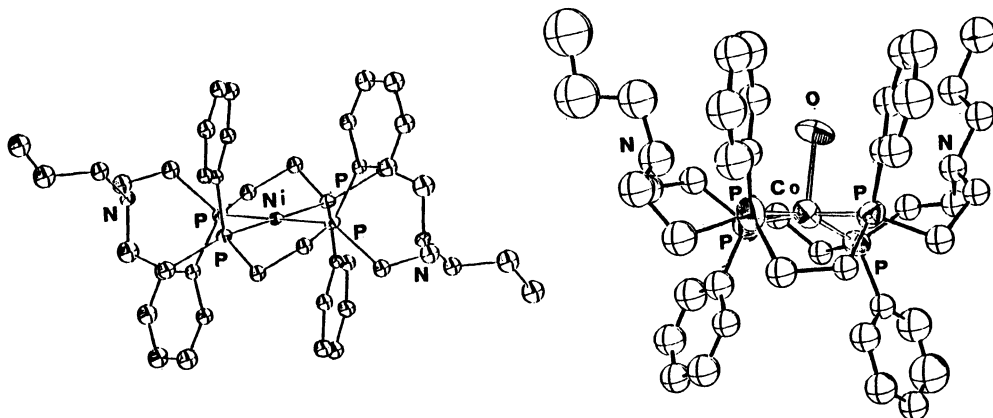


Fig. 8. Views of $|\text{Ni}(\gamma\text{-P}_4\text{N}_2)|^{2+}$ (left) and $|\text{Co}(\text{H}_2\text{O})(\gamma\text{-P}_4\text{N}_2)|^{2+}$.

It is now interesting to observe the stereochemical changes which occur in the metal complexes by substituting sulfur for oxygen in the above macrocycle. Thioether sulfur, being a softer donor than ether oxygen, is expected to be more strongly binding and more competitive with phosphorus toward coordination of soft metal ions. A non-planar arrangement of the four phosphorus atoms may occur in metal complexes, thus also allowing a different denticity to a given isomer with respect to that exhibited with a planar P_4 arrangement. Actually, this has been found with the δ - and ϵ -isomers of P_4S_2 . In the nickel(II) complex of δ - P_4S_2 a moiety $P...S...P$ adopts a meridional configuration but, in contrast with the ether analogue, the other chain $P...S...P$ brings the sulfur atom 3.59 Å away from the metal and it causes the P-Ni-P angle to decrease from 180° to about 138° (Figure 9).¹⁸ The planar arrangement of the four phosphorus atoms no longer occurs and the stereochemistry of the metal atom is well described as five-coordinate trigonal bipyramidal. Essentially the same stereochemistry holds for the cobalt derivative as proven by the electronic spectrum of the compound.¹⁸

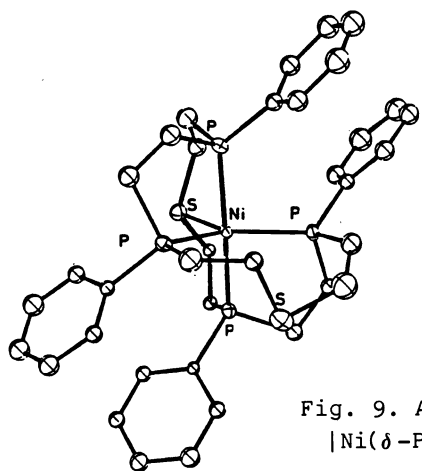


Fig. 9. A view of $|\text{Ni}(\delta\text{-P}_4\text{S}_2)|^{2+}$

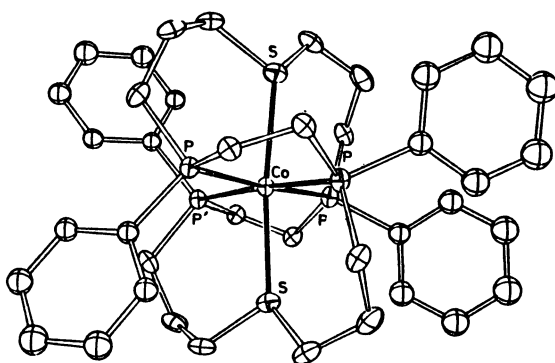


Fig. 10. A view of $|\text{Co}(\delta\text{-}|\text{22P}_4\text{S}_2)|^{2+}$.

The lower denticity of the δ - P_4S_2 macrocycle in these complexes with respect to the δ - P_4O_2 one may probably be a consequence of the high energies of the d^7 and d^8 configurations in octahedral low-spin coordination. The absence of documented examples with nickel(II) and the paucity of those with cobalt(II) may be attributed to the strong antibonding character of the e^* orbitals in octahedral coordination with such strong donors as those required to induce low-spin behaviour. With cobalt(II), for instance, assuming only σ -donor capabilities, such octahedral complexes are 19-electron species which thus can gain some energy stabilisation by a moderate increase of the axial and/or equatorial bond distances. Furthermore, such species should distort due to the operation of the Jahn-Teller effect and, in fact, elongated or compressed octahedral geometries have always been found.¹⁹ Otherwise, the more usual five-coordinate 17-electron species occur. Analogous considerations hold true for the nickel(II) complexes. Another way to overcome the antibonding character of the d_z orbital is to use weak axial donors. Both conditions apply to the six-coordinate $|\text{Co}(\delta\text{-P}_4\text{O}_2)|^{2+}$ ion where the two weak ether donors occupy axial positions at rather long bond distances (2.32 Å). With the stronger thioether donors of δ - P_4S_2 , longer M-S distances cannot be achieved in an octahedral complex due to the mer-conformation of the $P...S...P$ chains.

Further evidence of electronic inhibition to six-coordination of δ - P_4S_2 is shown by the behaviour of the δ -isomer of $|\text{22P}_4\text{S}_2$. Indeed, in the $|\text{Co}(\delta\text{-}|\text{22P}_4\text{S}_2)|^{2+}$ ion, the cobalt atom is here trans-octahedrally coordinated^{4b2} by the four phosphorus and the two sulfur atoms of the ligand.²⁰ Obviously, the $P...E...P$ moieties adopt mer-arrangements as it is found with the $|\text{Co}(\delta\text{-P}_4\text{O}_2)|^{2+}$ ion (Figure 10). The two Co-P bond distances of 2.295 Å are normal but slightly longer values than those (2.25 Å) found with other

polyphosphamacrocycles. The two Co-S distances of 2.52 Å are significantly longer than the Co-P bonds (in spite of the similar covalent radii of sulfur and phosphorus), making the coordination octahedron an elongated one. Apparently, longer trimethylenic chains of $|22|P_4S_2$ vs. P_4S_2 allow longer Co-S distances to be reached than dimethylenic ones in spite of the hindrance of meridionally arranged P...E...P chains.

With the ϵ -isomer of $|22|P_4S_2$ the cobalt(II) complex is low-spin and cis-octahedrally coordinated^{4,21} (Figure 11). Severe distortions of the coordination polyhedron are found both in the equatorial angles P-Co-P (127.7°) and S-Co-S (75.1°) and in the distances, with the axial Co-P bonds clearly shortened in comparison with the other four in-plane distances. In particular, the Co-S bond distances appear to be rather long, their mean value of 2.59 Å being longer by 0.08 Å with respect to the value found in the trans-octahedral $|\text{Co}(\delta\text{-}|22|P_4S_2)|^{2+}$ ion. Angular distortions in this structure may be attributed to large²¹ overcrowding of the ligand phenyl groups and to their stacking interactions.

With the remaining α - and γ - P_4S_2 isomers, the cobalt and nickel complexes do not show significant stereochemical differences with respect to those of the α - and γ - P_4O_7 .^{7,21} Actually, the denticity of these two isomers (five and four, respectively) cannot increase since it depends on geometrical factors. Furthermore, it seems unlikely that sulfur be preferred to phosphorus as a donor.

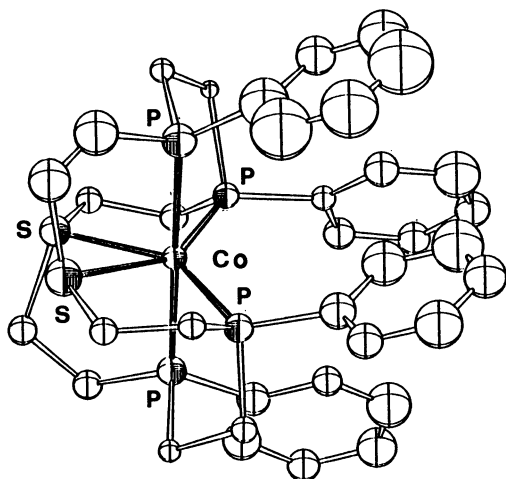


Fig. 11. A view of $|\text{Co}(\epsilon\text{-}P_4S_2)|^{2+}$

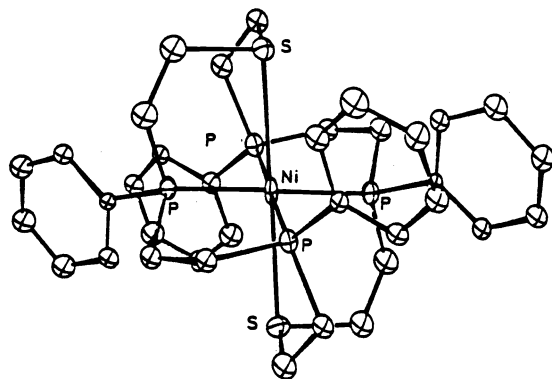


Fig. 12. A view of $|\text{Ni}(\beta\text{-}P_4S_2)|^{2+}$.

Finally, the stereochemistry of the $|\text{Co}(\beta\text{-}P_4S_2)|^{2+}$ ions, as inferred from their electronic spectra, appears to be a distorted octahedral one, probably resembling that of the ether analogue.⁵ On the other hand, the $|\text{Ni}(\beta\text{-}P_4S_2)|^{2+}$ is coordinated in a square-planar fashion by the four phosphano groups whereas the two thioether sulfurs point towards the axial coordination positions of the nickel (Figure 12). The Ni-S distances of 2.94 Å appear to imply some amount of nickel-sulfur interaction; this evidence is also shown by the electronic spectrum which neatly differs from those typical of square-planar nickel complexes.⁵

An interesting example of how the steric requirement of a given diastereoisomer complies with the electronic requirements of the metal

partner is given by the series of crystal structures on the complexes of $\beta\text{-P}_4\text{N}_2$ with iron(II), cobalt(II), and nickel(II) (Figure 13).²² The β -diastereoisomer is particularly suitable to follow subtle changes in the M...E interactions owing to the facial arrangement of the P...E...P moieties when it wraps the metal ion in a *trans*-octahedral fashion. This allows quite gradual variations in metal-nitrogen distances by slight conformational changes within $\text{E}|\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2|_2$ chains.

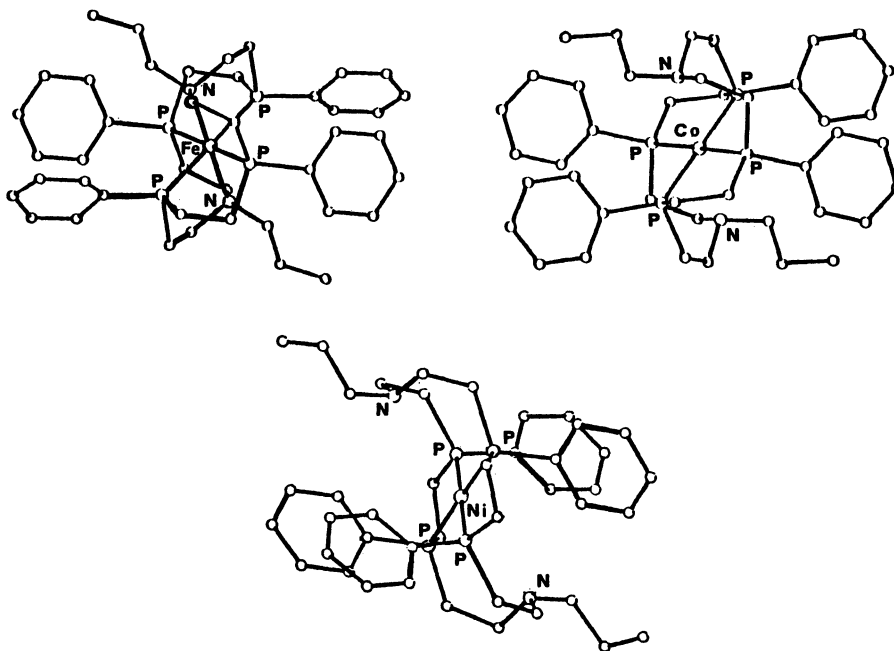


Fig. 13. Views of the cations $[\text{Fe}(\beta\text{-P}_4\text{N}_2)]^{2+}$, $[\text{Co}(\beta\text{-P}_4\text{N}_2)]^{2+}$, and $[\text{Ni}(\beta\text{-P}_4\text{N}_2)]^{2+}$.

It appears that the nitrogen atom is progressively rejected from the metal coordination sphere as the formal number of d electrons at the metal increases from six to eight. Indeed, the M-N distances jump from 2.23 Å in $[\text{Fe}(\beta\text{-P}_4\text{N}_2)]^{2+}$ to 2.63 Å in $[\text{Co}(\beta\text{-P}_4\text{N}_2)]^{2+}$ and to 3.30 Å in $[\text{Ni}(\beta\text{-P}_4\text{N}_2)]^{2+}$. The last value is quite indicative of non-bonding interactions whereas the first one surely indicates a real bond, the situation in the cobalt complex being an intermediate one. There is little doubt that the observed reduced ligational capabilities of the nitrogen atoms in the cobalt and nickel complexes be electronic in nature. They may be rationalized in terms of electron counts at the metal in these low-spin complexes. Indeed, with the iron complex a stable 18-electron species is found whereas with the nickel analogue a four-coordinate 16-electron species is highly stabilized by the square-planar P environment. The situation is a more ambiguous one with the cobalt(II) complex, for which it would be hard to make a guess among a 15-electron square-planar, a 17-electron square-pyramidal, or an improbable 19-electron octahedral species. The crystal data suggest the occurrence of two weak Co-N interactions if one considers the gradual evolution from the iron to the nickel structures.

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