

Spontaneous assembly of double-stranded helicates from oligobipyridine ligands and copper(I) cations: Structure of an inorganic double helix

(molecular helicity/polynuclear metal complexes/self-organization)

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ABSTRACT Two oligobipyridine ligands containing two and three 2,2'-bipyridine subunits separated by 2-oxapropylene bridges have been synthesized and some of their complexation properties with metal ions have been investigated. In particular, with copper(I) they form, respectively, a dinuclear and a trinuclear complex containing two ligand molecules and two or three Cu(I) ions. In view of the pseudotetrahedral coordination geometry of Cu(I)-bis(bipyridine) sites and of NMR data indicating that the present complexes are chiral, one may assign to these dinuclear and trinuclear species a double-helical structure in which two molecular strands are wrapped around two or three Cu(I) ions, which hold them together. These complexes may thus be termed "double-stranded helicates." Determination of the crystal structure of the trinuclear species has confirmed that it is indeed an inorganic double helix, possessing characteristic features (helical parameters, stacking of bipyridine bases) reminiscent of the DNA double helix. This spontaneous formation of an organized structure by oligobipyridine ligands and suitable metal ions opens ways to the design and study of self-assembling systems presenting cooperativity and regulation features. Various further developments may be envisaged along organic, inorganic, and biochemical lines.

Molecular helicity is a fascinating property displayed by chemical and biological macromolecular structures such as the α -helix of polypeptides and the helical conformation of polymers (1, 2). Particularly well known is the double helix present in nucleic acids (3), whose structure, formation, and dissociation have been the subject of very extensive studies. Helicity has been analyzed for twisted chains of atoms (4) and its basic geometrical features are found in several types of small molecules (5, 6).

We report here results on a class of organic ligands of poly(2,2'-bipyridine)[‡] nature, which, by binding metal ions of specific coordination geometry, undergo spontaneous organization into a helical double-stranded, polymetallic complex, in effect an *inorganic double helix*, reminiscent of the double-helical structure of nucleic acids (3, 7).

Design Principle. Previous work on the dinuclear Cu(I) complex $[\text{Cu}_2(\text{pQP})_2](\text{ClO}_4)_2$ of a special quaterpyridine ligand, **pQP**, has shown that in this dimeric species, two **pQP** molecules bind two Cu(I) ions in a distorted tetrahedral coordination geometry, using a bipyridine subunit from each quaterpyridine chain (8); the two **pQP** molecules possess a twisted, chiral conformation and are wrapped around the two Cu(I) ions (Fig. 1). Related structural features may be found in some other dinuclear metal complexes (9, 10).

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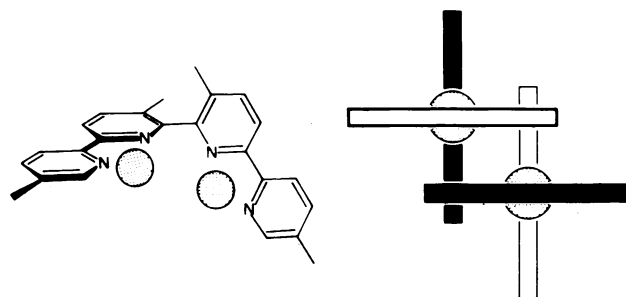
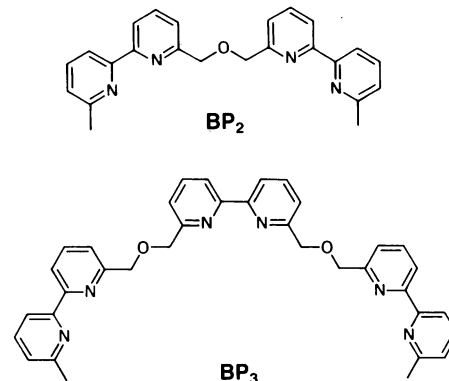


FIG. 1. (Right) Schematic representation of the dimeric complex cation $[\text{Cu}_2(\text{pQP})_2]^{2+}$ formed by two quaterpyridine ligands **pQP** and two Cu(I) ions; each bar represents a bipyridine moiety. (Left) Structural formula for a single **pQP** unit; see also ref. 8.

Suitable modification of the **pQP** ligand and extension of its basic features might lead to a general class of ligands capable of forming double-helical complexes. Rather than simply using polypyridine chains, it appeared desirable to preserve the basic bipyridine units in the ligand structure and to link several such groups by a bridge that would isolate the coordination sites from each other. In order to favor dimeric association as in the $[\text{Cu}_2(\text{pQP})_2]^{2+}$ complex (8), the bridge should be short enough to hinder tetrahedral binding of an ion by more than one bipyridine unit of the same ligand molecule and flexible enough to allow strain-free coordination in dimeric fashion. The simple $-\text{CH}_2\text{OCH}_2-$ group appeared to fulfill these requirements; note also that oligoethylene-glycol ligands may wrap around bound metal ions in a helical fashion (11, 12).

We herewith describe the synthesis and some metal ion complexation properties of the first two members, **BP**₂ and **BP**₃, of such a series of oligobipyridine ligands.

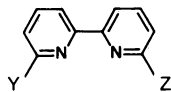


[‡]Throughout the text "bipyridine" ("bipy" in complexes) will be used for "2,2'-bipyridine."

MATERIALS AND METHODS

Chemicals. All chemicals used were high-purity commercial reagents.

Synthesis of the Polybipyridine Ligands BP₂ and BP₃.



- 1 Y = Z = CH₃
 2 Y = CH₃, Z = CH₂Br
 3 Y = Z = CH₂Br
 4 Y = CH₃, Z = CH₂OH
 5 Y = Z = CH₂OH

Bromination of 6,6'-dimethyl-2,2'-bipyridine (1) with *N*-bromosuccinimide in refluxing CCl₄ in the presence of dibenzoyl peroxide gave the monobromide 2 and the dibromide 3 (13). The monoalcohol 4 was obtained in about 80% yield, by treatment of 2 with an aqueous solution of sodium carbonate at reflux for 3–5 hr. The bis(hydroxymethyl) compound 5 was obtained in a similar way from 3 (about 85% yield).

A solution of 4 (400 mg, 2 mmol) in tetrahydrofuran (50 ml) under argon was treated with sodium hydride at room temperature for 30 min. Then 1 equivalent of 2 was added as a solid in one portion and the mixture was stirred at reflux for about 12 hr. After evaporation of the solvent, the residue was heated in methanol at reflux for about 1 hr and the mixture was then left overnight in the cold (4°C); the deposit formed was filtered, giving the dimeric compound BP₂ in ≈60% yield; it may be purified by chromatography on silica with CH₂Cl₂ as eluent (colorless plates from ethanol; mp 188–189°C).

To a solution of 4 (300 mg, 1.5 mmol) in tetrahydrofuran cooled to –60°C (dry ice/methanol) under dry nitrogen, a solution (1.5 M) of butyllithium in hexane was added dropwise with a syringe until the color showed a sudden change from pale yellow to brown violet. The solution was allowed to warm to room temperature and treated at once with 0.3 eq of the dibromide 3 (175 mg, 0.5 mmol), and the mixture was stirred at reflux for about 18 hr. Considerable precipitation of very small, lustrous, white crystals had occurred in this time. After evaporation of the tetrahydrofuran under reduced pressure, the product was transferred in air to a filter by using methanol, washed well on the filter with methanol and then with diethyl ether, and finally dried at 100°C for 10 min (yield: 247 mg, 83%). Though of adequate purity for preparation of metal complexes, the material can be recrystallized from boiling chloroform (50 ml/20 mg) by addition of an equal volume of acetonitrile and slow cooling, giving small, colorless crystals of BP₃ (mp 227–229°C). Compounds BP₂ and BP₃ have low solubility in common solvents, chloroform being the best.

Preparation of the Copper(I) Complexes of Ligands BP₂ and BP₃. The copper(I) complexes of BP₂ and BP₃ have been obtained by treating a chloroform solution of the ligand (≈20 mM) with an acetonitrile solution containing a slight excess of Cu(I) salt (perchlorate or trifluoroacetate). They have also been prepared by adding an aqueous solution of Cu(II) salt to a suspension of BP₂ or BP₃ in acetonitrile followed by reduction with aqueous hydrazine. The deep orange-red characteristic of Cu(I)-bipyridine complexes appeared immediately. It was not necessary to conduct the reaction under argon, since the resulting complexes are stable in air. Addition of ether precipitated the complexes as red solids in almost quantitative yield. They were redissolved in acetonitrile and an equal amount of water was added. The complexes [Cu₂(BP₂)₂]²⁺(CF₃COO[–])₂ and [Cu₃(BP₃)₂]³⁺(CF₃COO[–])₃ crystallized slowly as hydrates. The trifluoroacetate salts were soluble in a much wider range of solvents (CH₂Cl₂,

CHCl₃, CH₃CN, CH₃OH, acetone, ethanol, nitrobenzene, dimethylformamide, dimethyl sulfoxide, water) than the perchlorates and were therefore used preferentially.

All new compounds had spectral and microanalytical properties in agreement with their structure.

Determination of the Crystal Structure of [Cu₃(BP₃)₂](CF₃COO)₃. Crystals of the pentahydrate of this complex (C₇₈H₇₄O₁₅N₁₂F₉Cu₃, M_r = 1781.1) were grown from acetonitrile/water. They belong to the monoclinic space group *C*/2*c*, *a* = 23.283(2) Å, *b* = 19.614(2) Å, *c* = 36.187(2) Å, β = 108.35(1)°, volume = 15,685 Å³, Z = 8. We collected 5241 significant reflections (*I* > 3σ_{*I*}) on a Nonius CAD4 automatic diffractometer using Cu-K_α radiation and a crystal of approximate dimensions 0.45 × 0.20 × 0.20 mm. The structure was solved by using Patterson and Fourier techniques. All computations were performed with the Enraf–Nonius software package (14). Because of disorder the anions and water molecules could not be fully localized. Refinement with anisotropic temperature factors for the complex cation (91 atoms) led to an *R* factor of 14%. The space group is centrosymmetric; the crystal consists of a 1/1 mixture of the helices with opposite screw sense.

RESULTS AND DISCUSSION

Formation of Polymetallic “Double-Stranded Helicates.”

Bipyridine is a well-known chelating ligand that forms complexes with most metal ions and has been extensively studied for both its binding properties and the photoactivity of many of its transition metal complexes. Ligands BP₂ and BP₃ and analogues thereof may thus be expected to possess a rich coordination chemistry. Binding of Li⁺, Ag⁺, and Zn²⁺ was observed by the changes induced in the proton NMR spectra of the ligands on addition of a salt. However, most of the initial studies were done on Cu(I) and only these will be described here.

Binding of Cu(I) by ligands BP₂ and BP₃. Binding results in immediate formation of the deep orange-red characteristic of [Cu(I)(bipy)₂]⁺ and related units. The corresponding complexes, isolated and characterized as described above, may be formulated as the dinuclear [Cu₂(BP₂)₂]²⁺ and trinuclear [Cu₃(BP₃)₂]³⁺ species.

Nature of the Cu(I) complexes: Dinuclear and trinuclear double-stranded helicates. In view of the pseudotetrahedral coordination of the Cu(I) complexes of 6,6'-dimethylbipyridine (15) and quaterpyridine, pQP (8), as well as their high stability (16), it was expected that the complex of the “dimeric” ligand [Cu₂(BP₂)₂]²⁺ would have a structure similar to that of [Cu₂(pQP)₂]²⁺, with two Cu(I) ions bound to two bipyridine groups, one from each BP₂ molecule. By extension, it was surmised that the complex of the “trimeric” ligand [Cu₃(BP₃)₂]³⁺ would follow the same structural rule and therefore contain a double-helical strand of two ligand molecules wrapped around three “tetrahedrally” coordinated Cu(I) ions, as schematically represented in Fig. 2. These complexes present the features of an *inorganic double helix* and may be termed *double-stranded helicates* of Cu(I), designated by ds-ℳ_{*n*}, where *n* represents the number of metal centers M.[§] Such structures agree with the physicochemical properties of the complexes and were confirmed by determination of the crystal structure of the [Cu₃(BP₃)₂]³⁺ complex cation (see below).

Spectral and Physicochemical Properties. The *electronic absorptions* of the two complexes [Cu₂(BP₂)₂]²⁺ (λ_{max} = 449 nm, ε = 9800 M^{–1}cm^{–1} in CHCl₃) and [Cu₃(BP₃)₂]³⁺ (λ_{max} = 449 nm, ε = 14,600 M^{–1}cm^{–1} in CHCl₃) correspond to those

[§]The helical complexes of polyoxyethylene ligands are of single-strand type, ss-ℳ (see, for instance, ref. 11).

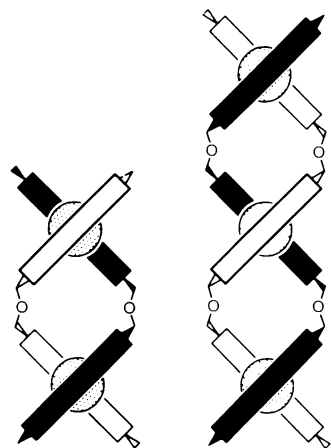


FIG. 2. Schematic representation of the double-stranded helicates formed by complexation of two and three copper(I) cations, respectively, by the oligobipyridine ligands BP_2 and BP_3 : $[\text{Cu}_2(\text{BP}_2)_2]^{2+}$ (Left) and $[\text{Cu}_3(\text{BP}_3)_2]^{3+}$ (Right). The right-handed helical form is shown; an idealized tetrahedral geometry has been used at each copper center.

expected for such Cu(I)-bipyridine complexes on the basis of the properties displayed by the $[\text{Cu}(\text{I})\text{-bis}(6,6'\text{-dimethylbipyridine})]$ complex ($\lambda_{\text{max}} = 454 \text{ nm}$, $\epsilon = 6700 \text{ M}^{-1}\text{cm}^{-1}$) (17) and by the dinuclear Cu(I) complex of the quaterpyridine pQP (see above) ($\lambda_{\text{max}} = 454 \text{ nm}$, $\epsilon = 12,700 \text{ M}^{-1}\text{cm}^{-1}$) (8).

The *proton NMR spectra* of the ligands BP_2 and BP_3 are markedly different from those of their Cu(I) complexes. The resonances of the bipyridine protons are shifted on complexation, but the most significant changes occur for the CH_2OCH_2 signals. Whereas these are singlets in the free ligands, they are shifted upfield by more than 1 ppm and split into AB patterns ($J \approx 13 \text{ Hz}$) in the complexes; two such patterns are present in the spectrum of $[\text{Cu}_3(\text{BP}_3)_2]^{3+}$ (Fig. 3). Thus, the CH_2 protons have become *nonequivalent* in the complexes, due to loss of the corresponding plane of symmetry. Fur-

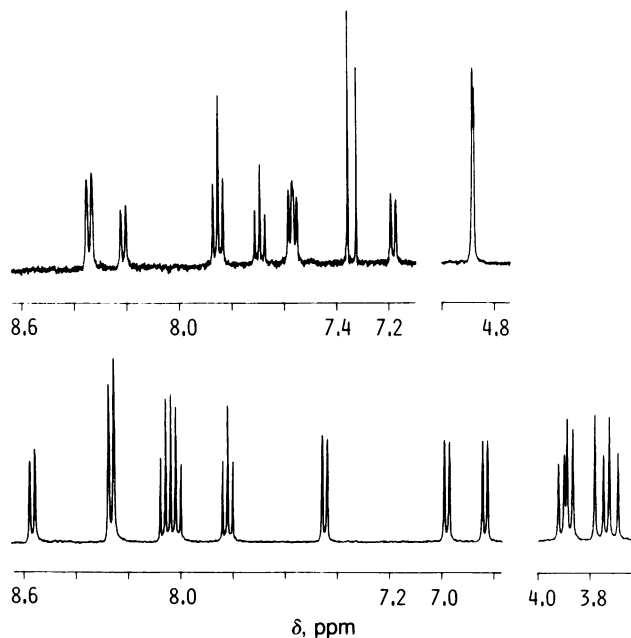


FIG. 3. The 400-MHz proton NMR spectra of the ligand BP_3 (Upper) and of the complex $[\text{Cu}_3(\text{BP}_3)_2](\text{CF}_3\text{COO})_3$ (Lower) in $\text{C}^2\text{H}_2\text{Cl}_2$; the CH_2 protons of the complex give two AB patterns around 3.8 ppm; the signal of the CH_2 protons of the ligand (two singlets at 4.88 ppm) is shown reduced by a factor of 2; CH_3 signal not shown.

thermore, their strong upfield shift indicates that they probably now lie in the shielding region of the bipyridine units.

Addition of excess chiral reagent anthracenyl-1-trifluoromethyl ethanol (18) to a $\text{C}^2\text{H}_2\text{Cl}_2$ solution of $[\text{Cu}_2(\text{BP}_2)_2]^{2+}$ produced partial splitting of the CH_2 AB pattern; a better-resolved splitting was obtained for the CH_3 signals of the $[\text{Cu}_2(\text{pQP})_2]^{2+}$ complex. These observations and the presence of CH_2 AB patterns show that the complexes are chiral, in agreement with their helical structure.

Since the CH_2 AB patterns are diagnostic of the complexes, the *kinetic stability* of the latter can be tested. Rapid exchange of the ligands (on the NMR time scale) should cause an $\text{AB} \rightarrow \text{A}_2$ conversion. Variable temperature proton NMR studies on the dinuclear complex $[\text{Cu}_2(\text{BP}_2)_2]^{2+}$ (in completely deuterated nitrobenzene) showed that the CH_2AB resonances (slow exchange separation of about 40 Hz at 200 MHz) moved together and broadened on heating, but coalescence was not attained at the highest temperature studied (393 K). If these changes result from ligand exchange and indicate the onset of coalescence, the barrier to this helix unravelling process should be greater than about 21 kcal/mol (1 kcal = 4.18 kJ), estimating the coalescence temperature to be at least 433 K. The barrier to such exchange should be even higher for the trinuclear complex $[\text{Cu}_3(\text{BP}_3)_2]^{3+}$, so that chiral resolution might be possible.

NMR and UV-visible titration experiments were performed by progressively adding a solution of $[\text{Cu}(\text{I})(\text{CH}_3\text{CN})_4]\text{ClO}_4$ in acetonitrile to a solution of BP_3 in chloroform. Only the free ligand and its tris-Cu(I) complex were observed over the whole titration range, going upwards from 0.1 eq Cu(I). This indicates a *positive cooperativity* in Cu(I) complexation, binding of an ion probably facilitating binding of the next one due to ligand preorganization. This interesting phenomenon deserves further study.

Crystal Structure of the $[\text{Cu}_3(\text{BP}_3)_2]^{3+}(\text{CF}_3\text{COO}^-)_3$ Complex: An Inorganic Double Helix. To confirm the structure assigned to the complexes described above and to more precisely assess their geometrical parameters, the crystal structure of the trinuclear complex $[\text{Cu}_3(\text{BP}_3)_2](\text{CF}_3\text{COO})_3$ was determined; three views are shown in Fig. 4.

It is seen that the $[\text{Cu}_3(\text{BP}_3)_2]^{3+}$ cation is indeed a double-stranded helicate (Fig. 4 Left) corresponding to the schematic representation given in Fig. 2 Left: two BP_3 ligand molecules are wrapped around each other and held together by three Cu(I) ions, which maintain the structure by metal coordination interactions as hydrogen bonding of base pairs maintains the double helix in nucleic acids. The schematic picture of Fig. 2 has molecular symmetry D_2 , in agreement with the NMR data for the complex in solution; of the three C_2 symmetry axes, one passes through the three copper ions, the other two are perpendicular to the first one through the central ion, one lying in the plane of the figure and the other perpendicular to it. This is not the case for the solid-state structure, as shown by Fig. 4 Center and Right. Whereas the planes of three bipyridine groups are parallel (Fig. 4 Center) those of the other three are not (tilt angle $\approx 27^\circ$) (Fig. 4 Right); as a consequence only one C_2 axis is conserved, that perpendicular to the plane of Fig. 2. In addition, a *dynamic helix bending-twisting process* must be present in solution, exchanging the three parallel bipyridines with the other three and conferring average D_2 molecular symmetry. Finally, this overall curvature of the double helix has analogies with that found in curved DNA (7, 19) and with the start of a super turn, such as found in supercoiled DNA (7).

The *helical features* (Fig. 4 Left) of each strand are defined by a total length of $\approx 16.5\text{--}17 \text{ \AA}$ (between terminal CH_3 groups) for about 1.5 turn, a pitch (length per turn) of $\approx 12 \text{ \AA}$, a radius of $\approx 6 \text{ \AA}$ for the circumscribed cylinder. A turn of the double helix contains two interaction centers, two metal ions.

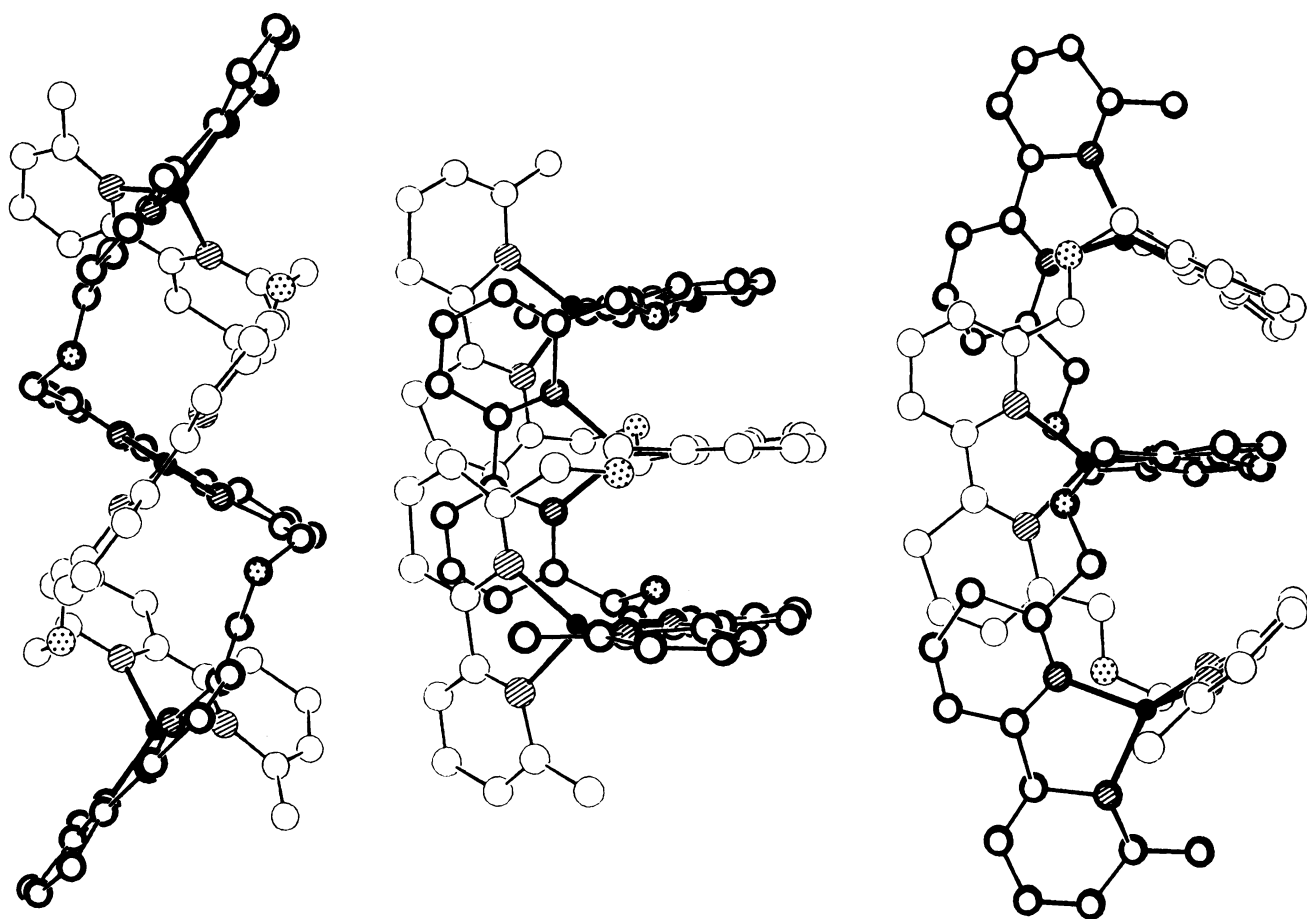


FIG. 4. Three views of the crystal structure of the double-stranded helicate complex $[\text{Cu}_3(\text{BP}_3)_2]^{3+}$; to facilitate perception of the structure one strand has been drawn in heavy lines; solid circles, Cu; hatched circles, N; stippled circles, O.

The two strands have the same chirality—i.e., screw sense. In comparison, the double helix of nucleic acids has a pitch of $\approx 30\text{--}35 \text{ \AA}$, an external radius of $\approx 10 \text{ \AA}$, and 10–11 base-pair interactions per turn (7).

One may also note that the double-stranded units formed by BP_2 and BP_3 (Fig. 2) as well as by pQP (Fig. 1) have the intertwined features of the “coupe du roi” (20) and of a braid with two threads and two or three crossings (21). Appropriate end-to-end connection of the threads of such type of dinuclear complexes may allow the synthesis of a molecular knot (C. O. Dietrich-Buchecker and J. P. Sauvage, personal communication).

The stacking of the bipyridine bases corresponds to a distance of 3.6 \AA between the planes of the parallel bases (Fig. 4 Center). The shortest distance between the nonparallel bipyridines (Fig. 4 Right) is $\approx 3.4 \text{ \AA}$, as expected for van der Waals contact, and is similar to the separation of stacked base pairs in DNA (7). The helix deformation affects markedly the overlap of the stacked bases: whereas the three nonparallel bases overlap by more than one full pyridine ring (bases at the left of Fig. 4 Center), the overlap of the three parallel bipyridines is reduced to about $\frac{1}{3}$ of a pyridine group (bases at the left of Fig. 4 Right). The bending of the overall structure may thus be due in part to the tendency of one set of three bipyridines to reach van der Waals contact and to overlap; another contribution might come from the length of the CH_2OCH_2 bridges separating the bipyridine units. Solid state deformation is not ruled out. The bipyridine stacking, although only partial, may nevertheless contribute to the stabilization of the double helix and favor its spontaneous assembly from the components.

The coordination properties of Cu(I) ions, which form pseudotetrahedral complexes with bipyridine and phenanthroline ligands (15, 22–24), induce the organization of the oligobipyridine ligands BP_2 and BP_3 . In the present complex, the three copper(I) centers have an almost identical, distorted tetrahedral coordination geometry. The Cu—N bond lengths (average of 2.02 \AA) and the N—Cu—N bond angles (two of 82° and four between 115° and 131°) are comparable to those of the bis(6,6'-dimethylbipyridine)·Cu(I) complex (15). The same is true for the dihedral angles (ca. 80°) between the planes of the two bipyridine units at each Cu(I) center. Since the Ag(I) complex of bis(6,6'-dimethylbipyridine) has a similar structure (25), it will be of interest to investigate the complex formed by BP_3 with Ag(I).

CONCLUSION

The results described above provide a general way for generating inorganic double-helical structures. The basic features of the present systems and the multiple potential variations in their structure allow us to imagine numerous extensions into a variety of directions.

From the point of view of general molecular features, these and related molecules offer an entry into the design of systems displaying self-organization, cooperativity, and helical chirality; they provide study cases for the mechanism, the thermodynamics, and the kinetics of formation and dissociation of a double helix in particular and a self-assembling system in general.

Variations in the basic organic structure of the ligands may involve (i) an increase in the number of subunits, by the synthesis of repetitive ligands BP_{n+2} , with extension to

polymeric ligands; (ii) the modification of ligand groups (for instance, replacing bipyridine by phenanthroline groups, etc.) and of intersite bridges; (iii) the introduction of substituents that are organized in the complexation process and bring their own properties.

From the point of view of *inorganic chemistry*, one may study the binding of other metal ions (possessing other coordination features), the formation of polymetallic chain complexes, the photoactivity, electroactivity, and reactivity of multicenter Cu(I), Ru(II), Re(I), etc., complexes; thus, polyelectronic exchange and photoinduced charge separation may be envisaged with such "stringed" complexes.

From the *biological* point of view, the poly[Cu(I)] complexes of BP_{n+2} ligands such as BP_2 and BP_3 (or of their phenanthroline-containing analogues) may undergo multiple binding to DNA and perform thermal or light-induced strand cleavage (26–29) with special selectivity features, since these complexes could act as redox active and photoactive helicates; the same should hold for poly[Ru(bipy) $_2^+$] or poly[Ru(phen) $_2^+$] chain complexes derived from these and related polypyridine or polyphenanthroline ligands; various biologically active groups (purines and pyrimidines, amino acids, intercalators, etc.) may also be attached to the periphery of the subunits.

Finally, the structural and physical features of the present and related species may be of use in the design of molecular devices (30), taking advantage of cooperativity and self-assembly processes.

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