Synthesis and structure of the copper(I) complex

$$\text{[Cu(dppm)}(2,2\text{'-bipy})_2(\text{NO}_3)_2\]$$

Wang Dongmei, Yang Ruina*, Hou Yimin, Hu Xiaoyuan & Jin Douman

Henan Institute of Chemistry, Zhengzhou 450002, P.R.China
and State Key Lab of Coordination Chemistry, Nanjing University
210093, P.R.China

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Binuclear copper(I) complex [Cu(dppm)(2,2'-bipy)]_2(NO_3)_2 (I, dppm=Ph_2PCH_2PPh_2) has been synthesized by a ligand replacement reaction. X-ray crystal structure of the complex (I) shows that dppm coordinates as a bridging bidentate ligand, and 2,2'-bipy as a bidentate ligand to the Cu(I) atoms with tetrahedral structure. NO_3 behaves as a free ion in this newly prepared binuclear copper(I) complex. Crystals (I) are monoclinic P2_1/n, a = 1.4663(5); b = 1.3076(5); c = 1.9910(6) nm; β = 110.66(3)°, V = 3.5719 nm³; Z = 2, F(000) = 1536. Dc = 1.332 g cm⁻³. R = 0.06320, Rw = 0.08132.

Copper(I) displays wide diversity in its structural chemistry, with the copper coordination number ranging from two to four. Procedures to synthesize copper(I) complexes are of great interest because of the diversity of products resulting from almost the same methodology. In order to imitate the structure and functions of the active centers of oxidase enzymes which contain mono- and di-valent copper centers, artificial systems should be developed. Binuclear copper(I) complexes containing bidentate bridging ligands have been the focus of much investigation in the last few years. It has been pointed out and confirmed that the four-electron-donor diphosphine ligand Ph_2PCH_2PPh_2(dppm) is a very efficient bridging bidentate ligand. Many examples of binuclear complexes containing the eight-membered ring M(μ-dppm)M⁺ are known with a variety of metals, oxidation states and coordination geometries. In general, it contains trans-bound, bridging dppm ligands to give a planar M₂P₄ core structure with the two metal atoms held in close proximity to each other (regardless of whether a metal-metal bond is present or not). This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of M₂(dppm)₄ compounds. The group IIB metal monochelation(Cu⁺, Ag⁺ and Au⁺) imparts to the M₂P₄C₂ framework an eclipsed and a staggered conformation.

Copper(I) complexes can be obtained directly from copper(II) compounds by ligand reduction. The most important fact in this procedure is that there must be an excess of ligand to stabilize the state of the resulting copper(I). In the present paper we describe an easy way to synthesize copper(I) complexes using the diphosphine ligand, dppm, as ligand reductant, where dppm, acting as a bridging ligand, forms binuclear complexes. Structural results allowed us to interpret some solution properties of the dppm derivatives, such as molecular weight and conductivity measurements.

Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The compound [Cu(dppm)(NO_3)_2] can be prepared according to the literature procedure. All solvents were dried by standard methods and distilled under nitrogen prior to use. Elemental analyses were carried out using an ERBA-1106 instrument (Italy). Cu and the P contents were determined using a JA96-970 spectrometer. IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. Conductivity measurements were carried out in MeOH solutions thermostatted at 25°C using a Shanghai DDS-11A conductivity meter and DJS-I type platinum black electrode. Melting points were determined on an Electrothermal apparatus and are uncorrected. Room temperature ³¹P-NMR spectra were taken on a DPX-400 NMR spectrometer in CDCl₃ with 85% H_3PO₄ as external reference.

2,2'-bipyridine (2mmol, 0.312g) was added to a suspension of [Cu(dppm)(NO_3)_2](1mmol, 1.019 g) in MeOH(35 cm³). The mixture was stirred for 12 h when a yellow precipitate was obtained at room temperature. The product was collected by filtration and washed with MeOH and Et₂O. The product was recrystallized from dichloromethane and MeOH to obtain yellow crystals; yield: 69%. [Found: C, 63.53;
Fig. 1—The structure of the complex \([\text{Cu(dppm)(2',2'-bipy)}]_2(\text{NO}_3)_2\)

\(\text{H, 4.58; N, 5.85; P, 9.8\%; Cu, 9.8\%. Calc. for } C_{70}H_{60}N_6P_4O_{10}Cu_2: \text{C, 63.11; H, 4.51; N, 6.31; P, 9.3; Cu, 9.5\%}\). \(\text{\textsuperscript{1}H-NMR(}\delta, \text{ppm)}: \text{3.3(s, CH}_2\text{), 6.9-7.2(m, ph, dppm); 7.4-8.7(m, bipy). \text{\textsuperscript{31}P-NMR: } -9.9 \text{ppm.} \)

A single crystal of dimensions\((0.1\times0.1\times0.15\text{mm})\) of the title complex was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator and MoK\(_\alpha\) radiator\((\lambda=0.071073 \text{ nm})\). Unit-cell dimensions and intensity data were measured at room temperature. Reflections were collected using \(\omega/2\theta\) scans\(\text{(scan width } 1.00+0.35\tan\theta\text{), 4833 of which were considered unique and 2176 observed}[\ge3\sigma(I)]. \) No significant change was detected in the intensity of the three standard reflections. Lorentz, polarization and absorption corrections were applied to the intensity data\(\text{(empirical method, } \psi\text{-scan). The structure was solved by direct methods and Fourier syntheses. The structure was refined by the full-matrix least-squares method. Computations were performed using the SDP program on a PDP11/44 computer. Selected bond lengths and angles are given in Table 1.}

Crystal data: \(C_{70}H_{60}N_6P_4O_{10}Cu_2\), monoclinic \(P2_1/n\), \(a = 1.4663(5)\); \(b = 1.30676(5)\); \(c = 1.9910(6)\) \(\text{nm}\); \(\beta = 110.66(3)^\circ\), \(V = 3.5719 \text{ nm}^3\), \(Z=2\), \(F(000)=1536\), \(D_c=1.332 \text{ g cm}^{-3}\), \(R=0.06320\), \(R_w=0.08132\).

## Results and discussion

### Synthesis

The colour changes occurring during the preparation of the complex \([\text{Cu(dppm)(NO}_3)_2]_2\) correlate with the reduction of cupric nitrate by diphosphines(dppm) to form a white copper(I) complex. What is more interesting is that the weakly bonded nitrate ligand in the complex \([\text{Cu(dppm)(NO}_3)_2]_2\) can be easily replaced by other ligands. The compound \([\text{Cu(dppm)(NO}_3)_2]_2\) reacts with the ligand(2,2'-bipyridine) at room temperature to give the title complex \((1)\). As a result of this ligand substitution, binuclear copper(I) complex can be obtained with high yield. The elemental analysis of the complex \((1)\) agreed well with its formula. Conductance data\(\text{(acetone solution)}\) show that the complex \((1)\) exists as a 1:2 electrolyte, confirming its binuclear nature and the bridging character of dppm. The title complex is obtained as air-stable solids, and soluble in organic polar solvents, such as \(\text{CH}_2\text{Cl}_2\), DMF and CHCl\(_3\). When melted in air, the complex \((1)\) decomposed and turned blue.

### Spectroscopic characterization

The IR spectra\(\text{(in CsI)}\) of the complex \((1)\) exhibit the expected absorptions bands due to the dppm ligand at 1485s, 1186w, 1098m, 783m, 740s, 718m, and 690s \(\text{cm}^{-1}\). The band expected at \(1385 \text{ cm}^{-1}\) was not resolved in \((1)\) due to the presence of the very intense nitrate band in the same region. In the 1500-700 \(\text{cm}^{-1}\) range, the characteristic absorption bands of nitrate anion appear, exhibiting a broad band at ca.1380-85\(\text{cm}^{-1}\).

The electronic absorption spectra also give information concerning copper-ligand binding. Absorption peaks \(\lambda < 300 \text{nm}\) belong to \(\pi - \pi^*\) or \(n - \pi\) orbital transition of the ligands. The wide band\(365 \text{ nm}\) of the complex \((1)\) arises from MLCT absorption bands\(\text{(metal to ligand charge transfer transition). The absorption peak(365 nm) belongs to } d^{10} \rightarrow \pi^* \text{ orbital transition, because 2,2'-bipyridine has a lower } \pi^* \text{ antibonding orbital, electrons can transfer from copper(I) } d^{10}(T_{2g}) \text{ orbital to the } \pi^* \text{ antibonding empty orbital of the N coordination atom of 2,2'-bipyridine(MLCT peak). This phenomenon is characteristic of copper(I).}\)
Selected bond lengths (10⁻¹ nm) and angles (°)

<table>
<thead>
<tr>
<th>Distance</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-P(1)</td>
<td>2.229(4)</td>
</tr>
<tr>
<td>Cu-N(2)</td>
<td>2.117(12)</td>
</tr>
<tr>
<td>P(1)-C(21)</td>
<td>1.805(11)</td>
</tr>
<tr>
<td>Cu-P(2)</td>
<td>2.271(3)</td>
</tr>
<tr>
<td>Cu-N(1)</td>
<td>2.083(13)</td>
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<tr>
<td>P(1)-C(1)</td>
<td>1.84(2)</td>
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<tr>
<td>P(1)-C(11)</td>
<td>1.854(14)</td>
</tr>
<tr>
<td>N(1)-C(51)</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>N(1)-C(55)</td>
<td>1.35(2)</td>
</tr>
</tbody>
</table>

X-ray crystal structure

The molecular structure of (1) is depicted in Fig. 1. In the solid-state, it consists of a neutral dimeric molecular unit with the two copper atoms bridged by a pair of dppm ligands. This cation has an inversion center. In addition, each copper atom is terminally bound by a 2,2'-bipyridine in a bidentate fashion. Two copper atoms are doubly bridged by two dppm ligands to form an eight-membered \( \text{Cu}_2\text{P}_2\text{C}_2 \) ring. Each copper atom displays a four-coordinate form having \( \text{P}_2\text{N}_2 \) donors. The slightly distorted tetrahedral coordination around copper is completed by two nitrogen atoms from 2,2'-bipyridine ligand and two P atoms from dppm. The dihedral angle between the N(1)-Cu-N(2) and P(1)-Cu-P(2) planes is 84.2°.

The Cu-N distances [0.2083(13) and 0.2117(12) nm] and the Cu-P distances [0.2229(4) and 0.2271(3) nm] in (1) are in good agreement with the Cu-N length of 0.2114(7)-0.2136(8) nm and the Cu-P distances of 0.2234(3)-0.2286(3) nm found in \([\text{Cu}(\text{dppm})(\text{phen})\text{H}(\text{PF}_6)_2] \). The Cu-Cu separation of 0.4638(3) nm is significantly longer than the range of copper-copper bond lengths [0.2494(5) to 0.2674(5) nm] found in \([\text{H}_6\text{Cu}_6(\text{PPh}_3)_6(\text{DMF})] \), suggesting that the copper atoms in the present compound are not involved in metal-metal bonding interactions. The Cu---Cu separation of (1) is much greater than that in \([\text{Cu}(\text{dppm})(\text{NO}_3)_2](0.3170(4) \text{ nm}) \). This is because a conformation occurs in order to avoid close contact between the two coordinated bulky 2,2'-bipy ligands, resulting in a large separation of the copper pair.

The large P-Cu-P angle of 134.0(2)° in (1) is not simply ascribed to a restriction by the bridged form of dppm. Among the various \( \text{M}_2(\text{dppm})_2(\text{M}=\text{Cu}, \text{Ag} \text{ and Au}) \) frameworks, the staggered conformation tends to open the P-M-P angle than the eclipsed one (non-planar type). Hence, the P-Cu-P angle is largely associated with the conformation of the \( \text{M}_2(\text{dppm})_2 \) framework. The title complex, indeed, has a rare staggered framework. The P-Cu-P units in (1) are nonlinear. The P-Cu-P angle [134.0(2)°] in (1) is similar to the corresponding P-Cu-P angle of 134.34(9)° found in the related binuclear (dppm)₂ complex \([\text{Cu}(\text{dppm})(\text{phen})\text{H}(\text{PF}_6)_2] \).

Thus, each copper atom is four-coordinate, with phosphorus atoms from each of two bridging dppm ligands occupying two of the coordination sites, the nitrogen atoms from 2,2'-bipyridine occupying the third and the fourth. Structural studies involving binuclear (dppm)₂ species of other transition metals have been much less frequent but¹⁰, in general, also reveal the common trans binding of the two dppm ligands, linear P-M-P fragments, and planar \( \text{M}_2\text{P}_4 \) skeletal units. For the d¹⁰ complexes, however, the P-M-P units are distinctly nonlinear. X-ray structural characterization of the complex \([\text{Cu}(\text{dppm})(2,2'\text{-bipy})\text{H}(\text{NO}_3)_2] \), reported here, clearly reveals that the P-M-P angles in (dppm)₂ compounds are not restricted by steric crowding of the dppm phenyl rings. The P-Cu-P angles (134.0°) in (1), in particular, is larger than the corresponding P-M-P value [131.8(5)°] found in \([\text{Cu}(\text{dppm})(\text{NO}_3)_2] \).

In summary, the doubly bridged bis (diphenylphosphine) methane complex \([\text{Cu}(\text{dppm})(2,2'\text{-bipy})\text{H}(\text{NO}_3)_2] \) has been structurally characterized by single-crystal X-ray methods and found to contain folded \( \text{M}_2\text{P}_4 \) core structures. In addition, the weakly-coordinated unidentate nitrate groups in the complex \([\text{Cu}(\text{dppm})(\text{NO}_3)_2] \) are apparently labile; the nitrate can be replaced by other ligands. The flexibility of the \( \text{M}_2\text{P}_4 \) core and the coordinative unsaturation of the dimer are particularly intriguing in that these features should facilitate the uptake and binding of larger substrate species than presently possible with known \( \text{M}_2(\text{dppm})_2(\text{M}=\text{Rh, Ir}, \text{Pd, Pt}) \) complexes, which are generally restricted to a square-planar coordination.
geometry. In addition, the nature of \([\text{Cu}(\text{dppm})(2,2'\text{-bipy})_2]_3(\text{NO}_3)_2\) suggests yet another mode for the binding of other ligands by \(\text{M}_2(\text{dppm})_2\) complexes. The \([\text{Cu}_2(\text{dppm})_3]^{2+}\) unit should provide a very convenient entry point for the synthesis and study of such molecules\(^{11}\).

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References