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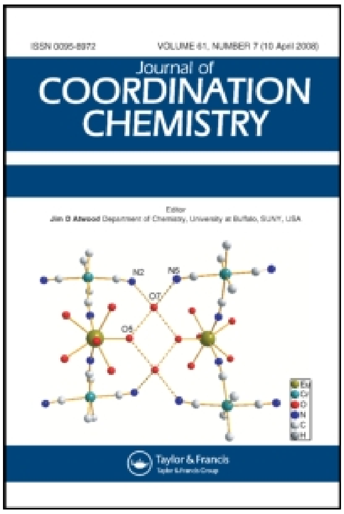

## Journal of Coordination Chemistry

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# PRECURSORS OF HEXA-AZAMACROCYCLES. SYNTHESIS AND X-RAY STRUCTURE OF 2,9-DIAMINOPHENANTHROLINEBISACETATE-Co(II) AND 6,6'-DIAMINOBIPYRIDINE-BISACETATE-M(II) (M = Ni, Cu)

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# PRECURSORS OF HEXA-AZAMACROCYCLES. SYNTHESIS AND X-RAY STRUCTURE OF 2,9-DIAMINOPHENANTHROLINE-BISACETATE-Co(II) AND 6,6′-DIAMINOBIPYRIDINE-BISACETATE-M(II) (M = Ni, Cu)

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The synthesis, conventional characterisations and x-ray structures of the following monomeric complexes are given for 2,9-diaminophenanthroline-bisacetate-cobalt(II) (A) and 6,6′-diaminobipyridine-bisacetate-M(II) (M = nickel(C) and copper(B)). Complex A crystalizes in the monoclinic, C2/c space group with $a = 12.813(6)$, $b = 10.218(3)$, $c = 13.811(5)$, Å; $\beta = 118.17(2)°$; Z = 4; V = 1549(2) Å$^3$. A total of 1787 unique reflections with $F > 6\sigma(F)$ were refined to values of R and $R_w$ 0.0461 and 0.0774, respectively. Complex B crystallizes in the triclinic, P-1 space group with $a = 10.099(5)$, $b = 10.257(5)$, $c = 8.015(11)$, Å; $\alpha = 112.98(2)$, $\beta = 93.13(2)$, $\gamma = 92.960(2)$,°; Z = 2; V = 761(1), Å$^3$. A total of 2603 unique reflections with $F > 3.00\sigma(F)$ were refined to values of R and $R_w$ 0.0764 and 0.1022, respectively. Complex C crystallizes in the monoclinic, $P2_1/n$ space group with $a = 8.124(5)$, $b = 10.343(6)$, $c = 18.724(11)$, $\beta = 98.36(2)$,°; Z = 4; V = 1556(1), Å$^3$. A total of 2537 unique reflections with $F > 3.00\sigma(F)$ were refined to values of R and $R_w$ 0.0689 and 0.0975, respectively. The structures consist of six-coordinate $[M(CH_3COO)_2(L)]$ (L = 2,9-diaminophenanthroline or 6,6′-diaminobipyridine) discrete monomeric neutral species, although in the Cu(II) compound the elongation of two long Cu—O bonds, due to the Jahn-Teller effect, makes the metal essentially four-coordinate. In the Ni and Co compounds the acetate acts as a bidentate ligand. The diamino ligands are coordinated by the pyridine nitrogen atoms. The IR spectra of the complexes have been

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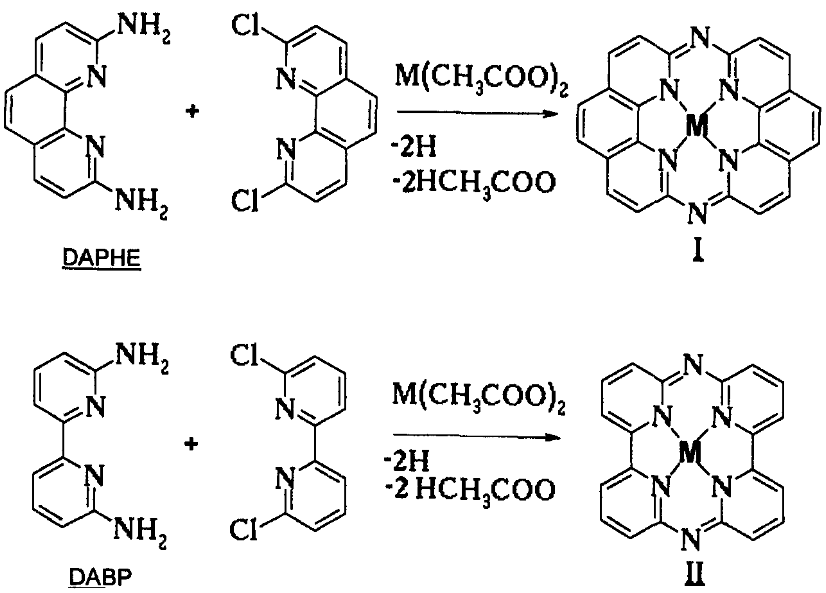
recorded and are discussed in relation to the crystal structure and the acetate coordination mode.

*Keywords*: Macrocyclic precursors; 2,9-diaminophenanthroline 6,6′-diaminobipyridine; Coordinated acetates

## INTRODUCTION

Aza-macrocyclic complexes such as I and II have gained importance in catalytic activation of small molecules, like carbon dioxide. Bis-bipyridine hexa-aza-macrocycles efficiently co-ordinate as tetradentate ligands, to give complexes of transition metal ions that are essentially planar [1a]. Spectroscopic, electrochemical and chemical characterizations of these systems have been published [1b]; electrochemical studies performed in a carbon dioxide atmosphere renders information about its electrocatalytic reduction. Quantum chemical calculations were also used to understand the origin of the properties of both the ligands and the metal complexes.[1b]. Diamino-phenanthroline (**DAPHE**), and diamino-bipyridine (**DABP**), are precursors in the synthesis of I and II, respectively, as shown in the Scheme (M = Co, Ni, Cu).



SCHEME Hexaazamacrocycles synthesised from 2,9-diamino-phenathroline and 6,6′-diamino-2,2′-bipyridine.

The yield for macrocyclic products is increased by performing the synthesis in two steps: (a) the formation of an acyclic diaminobipyridine- (or diamino-phenanthroline-) acetate complex, followed by (b), a template reaction between the intermediate obtained in (a) with the corresponding dichloro precursor. So, for complexes [Co(**DAPHE**)($CH_3COO)_2$] and [M(**DABP**)($CH_3COO)_2$] (M = Ni, Cu) prepared in step (a), infrared characterization and structure determination by single crystal x-ray diffraction has been performed. Distortions from regular octahedral, coordination modes of the acetate and a comparison of these structures are presented and discussed below.

## EXPERIMENTAL

### Instruments

Solid FTIR spectra were recorded using a Bruker IFS-66V spectrophotometer as KBr pellets in the 4000–400 $cm^{-1}$ and polyethylene pellets in the 400–150 $cm^{-1}$ ranges. Spectra were scanned with a resolution of 2 $cm^{-1}$. Scans (100) were accumulated for both the mid-FTIR and the far-FTIR measurements. Typical spectra are shown in Figures 1 and 2. UV-vis solid spectra(Nujol mull) were registered in a K.Zeiss DMR-22 spectrophotometer. UV-vis spectra in N,N′-dimethylformamide solutions were recorded in a Varian Cary 1E spectrophotometer. Cobalt, nickel and copper elemental analyses were performed with a Perkin-Elmer 2380 atomic absorption spectrophotometer.

### Synthesis

The reagents and solvents employed in the synthesis were analytical grade and were used without further purification. The synthetic procedures for diamino compounds are based mainly on the literature [2], with some modifications. [(DABP)Cu($CH_3COO)_2$], % Cu: Calc., 17.3; Exp., 17.2, Color, blue-green. [(DABP)Ni($CH_3COO)_2$], % Ni: Calc., 16.2; Exp., 16.6; Color, green. [(DAPHE)Co($CH_3COO)_2$], % Co: Calc., 14.1; Exp., 13.8; Color, red.

### X-ray Structure Determination

A summary of selected crystallographic data for complexes A, B and C is given in Table I.

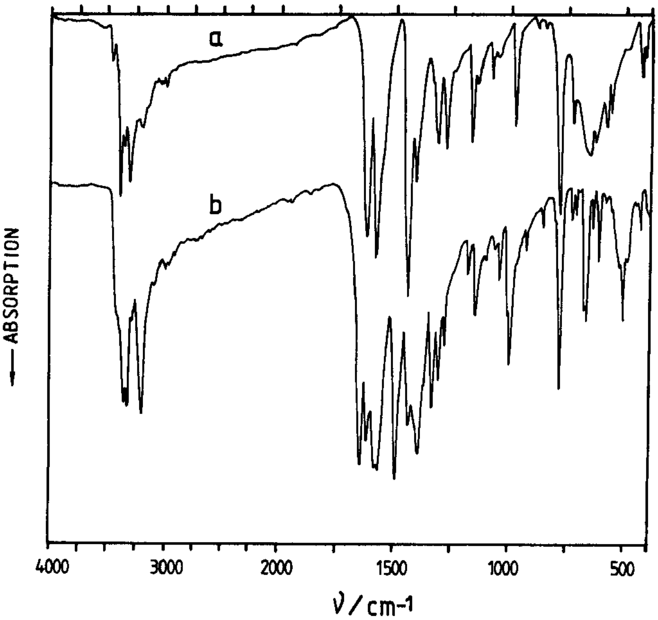


FIGURE 1 Infrared spectra of (a) the ligand DABP, and (b) the copper(II) complex in the spectral region 4000–400 cm$^{-1}$.

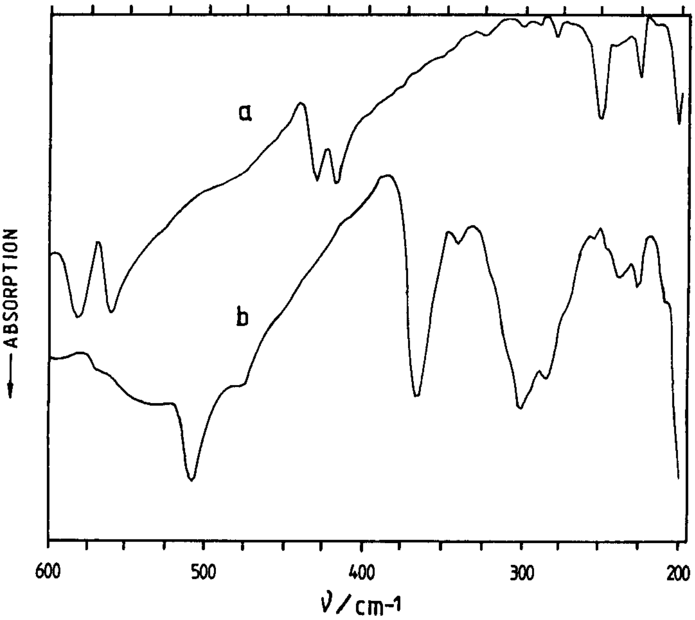


FIGURE 2 Infrared spectra of (a) the ligand DABP, and (b) the nickel(II) complex in the spectral region 600–200 cm$^{-1}$.

TABLE I Summary of crystal data and structure refinements

| | *A* | *B* | *C* |
|---|---|---|---|
| Chemical Formula | C16H16N4O4Co | C14H16N4O4Cu | C14H16N4O4Ni |
| Formula Weight | 387.26 | 367.85 | 363.02 |
| Temperature/K | 298 | 298 | 298 |
| Wavelength/Å | 0.71069 | 0.71069 | 0.71069 |
| Crystal System | Monoclinic | Triclinic | Monoclinic |
| Space Group | C2/c (N°15) | P-1 (N°2) | $P2_1$/(N°11) |
| A/Å | 12.813(6) | 10.099(5) | 8.124(5) |
| B/Å | 10.218(3) | 10.257(5) | 10.343(6) |
| C/Å | 13.811(5) | 8.015(11) | 18.724(11) |
| $\alpha$/° | | 112.97(2) | |
| $\beta$/° | 118.17(2) | 93.13(2) | 98.36(2) |
| $\gamma$/° | | 92.960(2) | |
| V/Å$^3$ | 1549(2) | 761(1) | 1556(1) |
| Z | 4 | 2 | 4 |
| Dcalc/Mg.m-3 | 1.614 | 1.606 | 1.55 |
| O/cm − 1 | 11.53 | 15.2 | 12.731 |
| F(000) | 796 | 378 | 752 |
| Crystal Habit | Prism | Bioc | Prism |
| Crystal Size/mm | 0.15 x 0.20 x 0.25 | 0.15 x 0.28 x 0.32 | 0.20 x 0.25 x 0.30 |
| Crystal Color | Pink | Blue | Green |
| 2Θmax/° | 60 | 60 | 60 |
| Index Ranges | $0 < h < 16$;<br>$0 < k < 14$;<br>$-17 < l < 12$ | $0 < h < 13$;<br>$-13 < k < 13$<br>$-10 < l < 10$ | $0 < h < 11$;<br>$0 < k < 14$;<br>$-24 < l < 26$ |
| Scan Speed/°.min − 1 | 2 | 2.5 | 4.5 |
| Transmission Factors | 0.77-1.00 | 0.82-1.00 | 0.81-1.00 |
| Scan Range/° | 1.1, 1.1 | 1.1, 1.3 | 1.2, 1.3 |
| Measured Reflections | 2552 | 3686 | 4286 |
| Unique Reflections | 2242 | 3571 | 3557 |
| Refined Reflections[1 > 3σ(1)] | 1787 | 2603 | 2537 |
| Refined Parameters | 123 | 208 | 220 |
| Decay/% | none | 1.22 | None |
| R$^a$ | 0.0461 | 0.0764 | 0.0689 |
| Rw | 0.0774 | 0.1022 | 0.0975 |
| S$^b$ | 0.98 | 0.955 | 0.955 |

A: [Co(2,9-diamino-1,10-phenanthroline)$(CH_3COO)_2$], B: [Cu(6,6′-diamino-2,2′-bipyridine)$(CH_3COO)_2$], C: [Ni(6,6′-diamino-2,2′-bipyridine)$(CH_3COO)_2$],

[a] $R(F) = \Sigma(Fo - Fc)/\Sigma Fo$,

[b] $S = [\Sigma\{(Fo^2 - Fc^2)^2\}/(n - p)]^{0.5}$; n = no. of Data and p = no. of refined parameters.

Data collections were carried out on a Syntex Diffractometer (modified by Crystallogic) using graphite-monocromated Mo-$K_\alpha$ ($\lambda = 0.71069$ Å) radiation at 292 K. For the three complexes, determination of the crystal class, orientation matrix and cell dimensions were performed according to established procedures; the intensity data were collected using $2\theta-\theta$ scan mode. Three standard reflections were monitored after every one hundred data measurements, showing only small random variations (< 1.5%). Absorption was analyzed with psi-scan. The data were processed with the

Crystallogic program package [3] that is, for absorption, Lorentz and polarization effects. Most of the non hydrogen atoms in complexes A, B and C were located by direct methods with SIR program package [4] and subsequent Fourier syntheses [5] were used to derive the remainder. All non-H atoms were refined anisotropically [5]. Hydrogen atoms of the ligands were generated geometrically (C—H 0.96 Å), except for some that were obtained from difference Fourier maps, assigned isotropic thermal parameters, allowed to ride on their parent carbon atoms and included in the final stage of full matrix least square refinement using 2242, 3571 and 3557

TABLE II

| | | | |
|---|---|---|---|
| Bond lengths(Å) with E.S.D.'S in parentheses | | | |
| Co—O2 | 2.254(2) | Co—N1 | 2.082(3) |
| Co—O1 | 2.109(2) | | |
| Cu—O1 | 2.536(6) | Cu1—N1 | 1.989(6) |
| Cu—O2 | 2.005(5) | Cu1—N7 | 2.003(5) |
| Cu—O3 | 1.961(6) | | |
| Cu—O4 | 2.638(6) | | |
| Ni—O1 | 2.081(5) | Ni—N1 | 2.035(5) |
| Ni—O2 | 2.131(5) | Ni—N7 | 2.051(5) |
| Ni—O3 | 2.185(5) | | |
| Ni—O4 | 2.088(4) | | |
| Bond angles(°) with E.S.D.'S in parentheses | | | |
| O1—Co—N1 | 104.0(1) | O1—Co—O1′ | 163.0(1) |
| O2—Co—N1 | 163.4(1) | N1—Co—N1′ | 81.3(1) |
| O2—Co—O1 | 60.0(1) | C2—N1—Co1 | 112.0(2) |
| O2′—Co—N1 | 98.0(1) | C6—N1—Co1 | 129.4(2) |
| O1′—Co—N1 | 105.0(1) | | |
| O3—Cu—O1 | 93.1(2) | N7—Cu—O1 | 100.7(2) |
| O2—Cu—O1 | 56.2(2) | N7—Cu—O3 | 98.3(2) |
| O2—Cu—O3 | 89.3(2) | N7—Cu—O2 | 156.2(2) |
| O4—Cu—O1 | 134.0(2) | N7—Cu—O4 | 114.2(2) |
| O4—Cu—O3 | 54.4(2) | N7—Cu—N1 | 82.2(2) |
| O4—Cu—O2 | 88.6(2) | C2—N1—Cu | 114.8(5) |
| N1—Cu—O1 | 107.8(2) | C6—N1—Cu | 126.8(4) |
| N1—Cu—O3 | 158.7(2) | C8—N7—Cu | 113.5(5) |
| N1—Cu—O2 | 98.7(2) | C12—N7—Cu | 127.7(4) |
| N1—Cu—O4 | 105.8(2) | | |
| N7—Ni—N1 | 80.7(2) | O4—Ni—N1 | 103.4(2) |
| O1—Ni—N1 | 98.9(2) | O4—Ni—N7 | 95.9(2) |
| O1—Ni—N7 | 105.1(2) | O4—Ni—O1 | 151.5(2) |
| O2—Ni—N1 | 161.0(2) | O4—Ni—O2 | 95.2(2) |
| O2—Ni—N7 | 101.4(2) | O4—Ni—O3 | 60.9(2) |
| O2—Ni—O1 | 62.2(2) | C2—N1—Ni | 114.4(4) |
| O3—Ni—N1 | 99.7(2) | C6—N1—Ni | 127.3(4) |
| O3—Ni—N7 | 156.4(2) | C8—N7—Ni | 113.2(4) |
| O3—Ni—O1 | 98.1(2) | C12—N7—Ni | 113.2(4) |
| O3—Ni—O1 | 85.9(2) | | |

unique reflections (for A, B and C, respectively) based on F. Selected bond lengths and angles are listed in Table II. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference numbers 141371/141372/141373.

## RESULTS AND DISCUSSION

### Spectroscopic and Magnetic Susceptibility

UV-Visible solid spectra show two important features in each of the three-complexes, namely (a) characteristic bands for octahedral Co(II), Ni(II) and Cu(II) in the region 500–750 nm, and (b) a medium intensity band at *ca.* 350 nm which can be assigned to the 6,6′-diamino-2,2′-bipyridine ligand coordinated in a cisoidal conformation as confirmed by x-ray structure determination [6]. $^1$H-NMR spectra could not be recorded due to the para-magnetic character of these compounds. Rough solid magnetic susceptibility values indicate that the species are monomeric and magnetically diluted.

The IR spectral analysis is focused on the characterization of the ligand and metal-ligand coordination. In this sense it is expected that bonds close to the metal coordination (CO and CN) will be most influenced by metal coordination. A list of the most relevant infrared frequencies of the acyclic complexes $[(DABP)M(CH_3COO)_2]$ (M = Cu, Ni), and $[(DAPHE)Co(CH_3COO)_2]$ is presented in Table III.

Most assignments were made by comparison with those of related ligands and complexes [7] and characteristic infrared group frequencies [8]. As expected, the spectral shape of the phenanthroline and bipyridine complexes is similar taking into account the similarity of both ligands.

The asymmetric CO acetate-stretching band at *ca.* 1550 cm$^{-1}$ and the symmetric mode at 1460 cm$^{-1}$ are ascribed to coordinated rather than ionic species. The frequency difference between these modes has been used to assign the acetate fragment as mono or bidentate [8(a)]. see Table IV.

The acetate group is bidentate ligand in $[(DABP)Ni(CH_3COO)_2]$ and $[(DAPHE)Co(CH_3COO)_2]$, while it is essentially monocoordinated in $[(DABP)Cu(CH_3COO)_2]$ [9, 10], as expected by the Jahn Teller effect [11–13]. Stretching vibrations of the $NH_2$ group localized in the region 3500–3100 cm$^{-1}$ remain at about the same frequency in the spectrum of the complexes, which indicates that the $NH_2$ group is not directly involved in

TABLE III Selected FT-IR Results for (a) DABP, (b) $[Cu(DABP)(CH_3COO)_2]$, (c) $[Ni(DABP)(CH_3COO)_2]$ and (d) $[Co(DAPH)(CH_3COO)_2]$

| *a* | *b* | *c* | *d* | *Assignment* |
|---|---|---|---|---|
| 3360 w | 3355 msd | 3364 msd | 3375 s | |
| 3311 m | 3325 | | 3325 w | $\nu NH_2 + \nu CH$ |
| 3208 w | 3201 s | 3212 s | 3212 s | |
| 1628 s | 1647 s | 1651 sd | 1653 s | |
| | | 1635 | 1625 vw | $\nu CN$ |
| | 1618 m | 1613 ms | 1607 w | |
| 1588 s | | | | |
| | 1567 sd | 1566 ms | 1559 msas. | $\nu_{as}COO + \nu CN$ |
| | | 1536 sb | 1530 w | |
| | 1493 vs | 1485 s | 1497 ms | $CH_3COO^-$ |
| 1447 vs | | | | |
| | 1436 m | 1453 sd | 1452 s | $\nu_{s.}COO + \nu CN$ |
| 1413 m | | | 1417 s | $\nu CC$ |
| | 1337 m | | 1348 w | $\delta CH_3$ |
| 1279 m | 1283 w | 1277 m | | $\nu CC$ |
| | 515 ms | 510 m | 507 ms | MO sens. |
| | 370 ms | 368 s | 375 ms | |
| | 291 w | 302 ms | 291 bs | MN sens. |

Relative intensity (abbreviations), *vs.* very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; d, double; as, asymmetric; sens, sensitive.

TABLE IV Acetate ligand in the complexes synthesised: asymmetric $\nu_a$ and symmetric ($\nu_s$) C—O stretching modes and mode of co-ordination#

| *Compound* | $\nu_{a(C=O)}$ | $\nu_{s(C-O)}$ | $\Delta_{a-s}$ | *Structure* |
|---|---|---|---|---|
| $[Cu(\mathbf{DABP})(CH_3COO)_2]$ | 1567 | 1436 | 131 | Unidentate |
| $[Ni(\mathbf{DABP})(CH_3COO)_2]$ | 1536 | 1453 | 83 | Bidentate |
| $[Co(\mathbf{DAPHE})(CH_3COO)_2]$ | 1530 | 1452 | 78 | Bidentate |
| $[RuCl(CH_3COO)CO(PPh_3)_2]$* | 1507 | 1465 | 42 | Bidentate |
| $[RuH(CH_3COO)(PPh_3)_2]$* | 1526 | 1449 | 77 | Bidentate |
| $[Pd(CH_3COO)_2(PPh_3)_2]_2$* | 1626 | 1314 | 315 | Unidentate |
| $CH_3COO^-$* | 1578 | 1414 | 164 | Ionic |

#$\nu$ in $cm^{-1}$.

* Data for some complexes has been included for comparison, see 8(a).

metal coordination, see Table III. Frequencies of vibrations involving the pyridinic N atoms are shifted by complexation, indicating that these N atoms are involved in metal coordination. CC bonds close to the coordinating atoms are less affected by coordination. The spectral modifications in the complexes suggest a $\pi$ electronic redistribution around the coordination site. In addition, medium intensity bands appearing at *ca.* 500, 350 and 300 $cm^{-1}$ in the complexes are assigned to vibrations involving the coordinating metal ions; the band *ca.* 300 $cm^{-1}$ is attributed to the MN stretching vibration and at least one of the other two bands could correspond to the νMO mode [14]. Other bands below 600 cm$^{-1}$ such as those about 580 and 420 cm$^{-1}$ assigned to ring deformations, disappear on complexation. This behavior is probably due to an anchorage effect caused by the metal ion; several vibrational movements are restricted or disappear upon complexation.

Crystallographic structures confirm these results and will be discussed next.

## Crystallographic Structures

Cu(II), Co(II) and Ni(II) acetate complexes with chelating nitrogen donors such as unsubstituted phenathroline and bipyridine have been synthesized recently. X-ray crystal structures of several dimeric Cu(II) acetate complexes with phenathroline, and bipyridine have been reported [15–18] where acetate acts as a monodentate ligand or a bidentate(bridge) between two

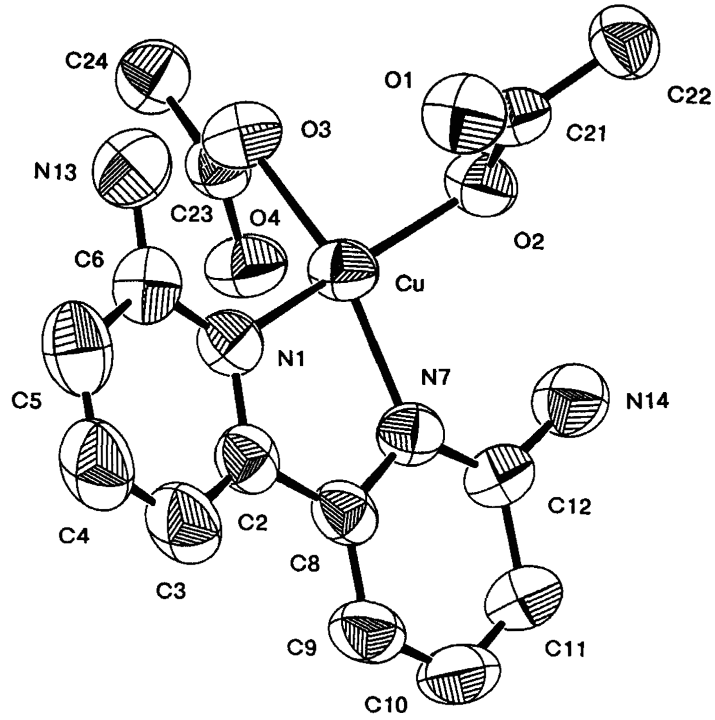


FIGURE 3 Cu(6,6′-diamino-2,2′-bipyridine)$(CH_3COO)_2$: molecular structure showing the numbering scheme. Displacement ellipsoids are drawn at the 50% of probability level.

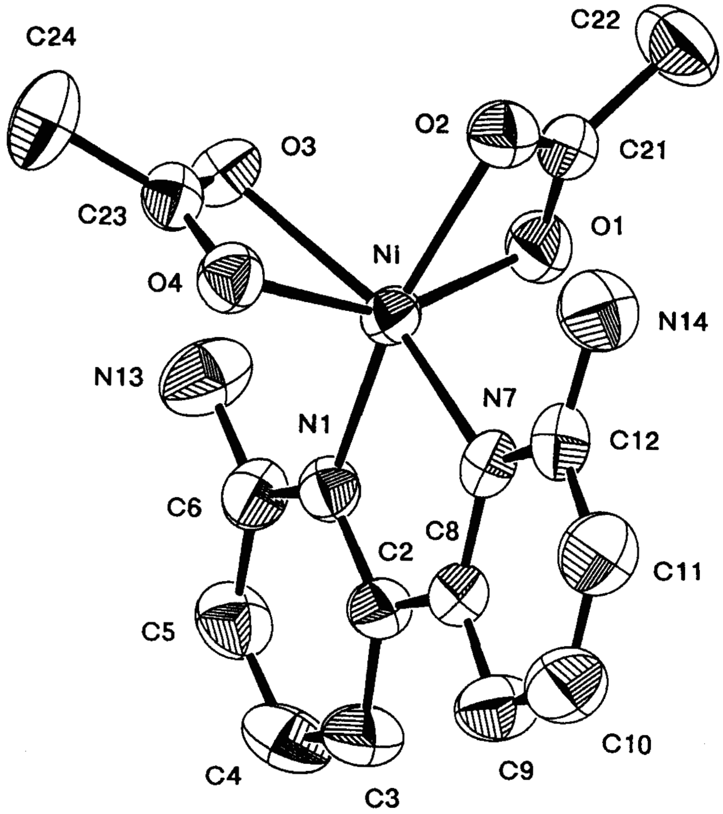


FIGURE 4 Ni(6,6′-diamino-2,2′-bipyridine)$(CH_3COO)_2$: molecular structure showing the numbering scheme. Displacement ellipsoids are drawn at the 50% of probability level.

copper atoms. Also, dinuclear Ni(II) complexes with bidentate acetate groups have been reported, but the ligand is an azamacrocycle [19–21].

On the other hand, monomeric Cu(II), Co(II) and Ni(II) complexes with these ligands have also been reported [22–24]. In some cases acetate acts as a chelating ligand,like carbonate [25] in monomeric complexes [12,26–31]. In most of these cases, both for monomeric and dimeric complexes the metal is six-coordinate and in general octahedral. Nevertheless, an x-ray derived tetrahedral structure with monocoordinated acetates [32,33] has been reported in the literature for some phenanthroline – or bipyridine-complexes of cobalt(II)-acetate.

## Description of the Structures

Figures 3, 4, and 5 depict the molecular structures of the three complexes. The lack of a M—N amine bond agrees with the UV-Vis and IR spectra. So,

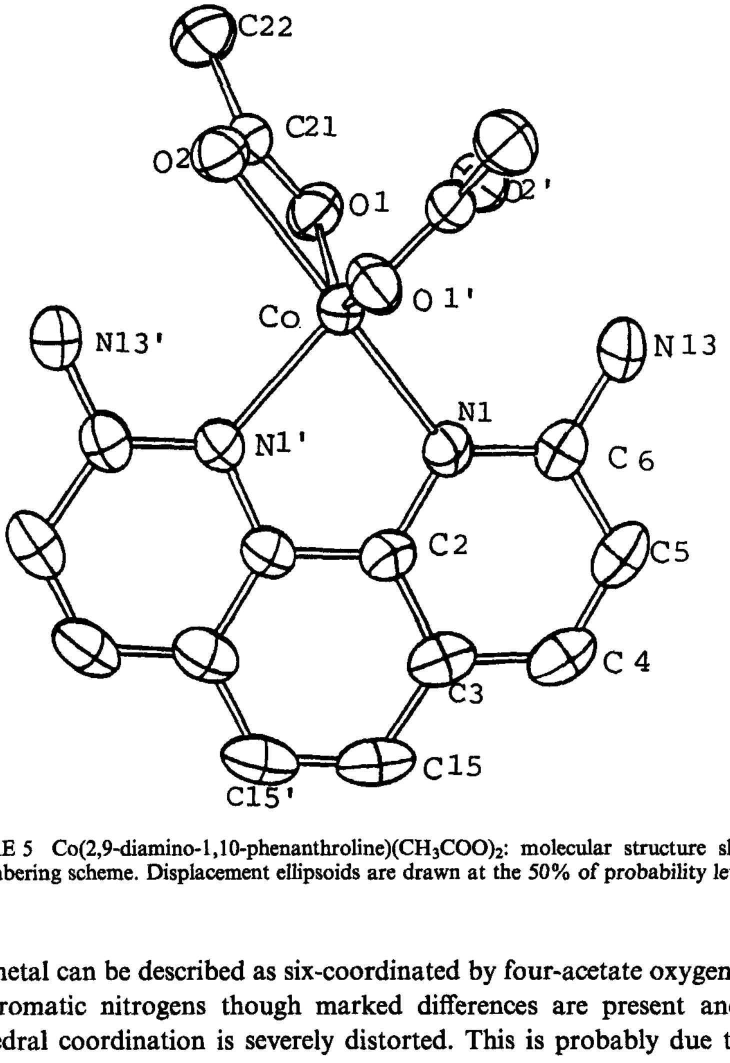


FIGURE 5 Co(2,9-diamino-1,10-phenanthroline)$(CH_3COO)_2$: molecular structure showing the numbering scheme. Displacement ellipsoids are drawn at the 50% of probability level.

each metal can be described as six-coordinated by four-acetate oxygens and two aromatic nitrogens though marked differences are present and the octahedral coordination is severely distorted. This is probably due to the chelating acetate whose anisobidentate effect decreases in the order Cu > Co > Ni. On the other hand the M—N bond, which increases its strength in the order Cu > Ni > Co, shows a small range of variation (1.989(6)–2.082(3) Å in comparison with a longer M—O range (1.961(6)–2.638(6) Å), see Table II. The octahedral deformation can be analyzed directly on the "*trans*" angles. Thus, the range of variation is 151.5°–160.0° (Ni), 140.5°–163.4° (Co) and 134.0°–158.7° (Cu), suggesting that the Ni complex has a more regular deformation whereas for the Cu complex it is less distorted, see Table II. In particular the "*trans*" angle O—M—O, 134°, for Cu is very far from an expected value of 180°; furthermore, the corresponding Cu—O bonds are elongated (2.536 and 2.638 Å ) suggesting a severe distortion due to the Jahn-Teller effect. Therefore, Cu is formally six-coordinate but essentially four-coordinate. In conclusion, the combination between a variable acetate anisobidentate effect, a rather stable nitrogen binding and the characteristic Jahn-Teller Cu(II) effect determine a structural trend where Ni and Cu are opposite and Co in between. In the Cu complex the O atom weakly coordinated to the metal forms a strong C—O bond as expected for a carbonyl moiety, such effect is also present but less pronounced in the Ni and the Co complex because of a more anisobidentate acetate in the Cu species.

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