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# Transition metal complexes of benzil-α-monoxime (BMO); X-ray structure determination of $Co(BMO)_3$

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**Abstract**

Cobalt(III), nickel(II) and copper(II) complexes of benzil-α-monoxime (BMO) have been synthesized and characterized by elemental analyses, conductivity, magnetic susceptibility measurements, IR and electronic spectral data. The molar conductivity data show them to be non-electrolytes. The monoanionic bidentate behavior of BMO is inferred from IR spectral studies. The electronic spectral data suggest planar geometry for nickel(II) and copper(II) complexes. The nickel complex assumes an octahedral structure in a coordinating solvent (*N*,*N*-dimethylformamide (DMF)). The $[Co(BMO)_3]$ complex has been isolated as a single crystal and its structure was determined by X-ray diffraction. X-ray data confirms the presence of a *fac*-octahedral configuration for this complex. Electrochemical studies suggest that the cobalt complex undergoes two single one-electron reduction steps corresponding to Co(III) → Co(II) and Co(II) → Co(I). © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Transition metal complexes; Electronic spectral data; Oximes; Benzil-α-monoxime

## 1. Introduction

Oximes are widely recognized ligands [1,2]. In general, monoxime is known to coordinate in three different ways (structures **I**, **II** and **III**). In structure **III** monoxime acts as a bridging ligand. Among carbonyl oximes diacetylmonoxime is the most studied ligand. Ni(II), Cu(II) and Co(III) complexes of diacetyl monoxime have been reported [3–5]. There is considerable confusion in the literature [6] about the nickel complexes of benzil-α-monoxime (BMO). Because of this, no report is available on Co(III), Ni(II) and Cu(II) complexes of BMO. In continuation of our ongoing research [7–11] on the metal complexes of benzil-based derivatives, we report herein the synthesis and characterization of metal complexes with BMO. The structure of $Co(BMO)_3$ is determined by X-ray single-crystal diffraction. Variety in structural features of BMO metal complexes is presented in this paper.

## 2. Experimental

### 2.1. Materials and methods

Benzil and hydroxylamine hydrochloride were of reagent grade. Solvents used for the synthesis of ligands and their metal complexes were redistilled. All other chemicals were of AR grade and used as supplied.

### 2.2. Preparation of ligand

BMO was prepared according to the procedure described previously [12].

### 2.3. Preparation of complexes

Attempts to prepare a cobalt(II) complex of BMO were not successful. Cobalt(III), nickel(II) and copper(II) complexes were prepared by mixing a hot methanolic solution of metal chlorides (1 mol) and ligand (2 mol). To the boiling solution of the ligand (0.01776 mol) in methanol (100 $cm^3$) was added metal chloride dissolved in a minimum quantity of methanol and refluxed for 30 min. NaOAc (2 g) was added to the

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Table 1
Analytical data of ligand and their metal complexes

| Ligand/complex | Color (m.p. ° C) | Percentage [a] of | | |
|---|---|---|---|---|
| | | Carbon | Hydrogen | Nitrogen |
| BMO | light pink | 74.00 | 4.57 | 6.50 |
| | (140–141) | (74.66) | (4.80) | (6.20) |
| $[Co(BMO)_3]$ | orange red | 68.20 | 4.15 | 5.70 |
| | (195–197) | (68.94) | (4.10) | (5.74) |
| $[Ni(BMO)_2]$ | light green | 65.95 | 3.72 | 5.48 |
| | (215–218) | (66.40) | (3.75) | (5.53) |
| $[Cu(BMO)]_n$ | dark green | 65.67 | 3.85 | 5.49 |
| | (175–177) | (65.75) | (3.91) | (5.47) |

[a] Calculated values are in parentheses.

reaction mixture (in the case of the copper complex $CH_3ONa$ is added) and refluxed for another 30 min. Crystalline complexes which separated from the solution were collected by filtration, washed with hot water and a small quantity of methanol and dried under vacuum over $CaCl_2$. The analytical data of the ligand and their complexes are presented in Table 1.

### 2.4. Physical measurements

The elemental microanalyses were carried out at the RSIC, CDRI, Lucknow, India. The molar conductance of the complexes in *N*,*N*-dimethylformamide (DMF) ($1 \times 10^{-3}$ M) solution were measured at 28°C with a Systronic model 303 direct reading conductivity bridge. Magnetic measurements were carried out in the polycrystalline state on a PAR model 155 vibrating sample magnetometer operating at a field strength between 2 and 8 KG. High purity Ni metal (saturation moment 55 emu $g^{-1}$) was used as a standard. The electronic spectra were recorded in DMF and $CHCl_3$ with a Shimadzu UV-160 A spectrophotometer. The FT-IR spectra were recorded in the range 4600–50 $cm^{-1}$ with a JASCO FT/IR-5300 in KBr and polyethylene medium. $^1H$ NMR spectra were obtained using a JEOL-GSX-400 NMR instrument at r.t. The voltammetric measurements were performed on Bio-analytical Systems (BAS) CV-27 assembly in conjunction with an X-Y recorder. These measurements were made on the degassed ($N_2$ bubbling for 5 min) solution in dimethylformamide ($1 \times 10^{-3}$ M) containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. The system consisted, working (glass carbon), an auxiliary (Pt wire) and reference (Ag/AgCl) electrodes.

### 2.5. X-ray crystallography and structure solution

A diffraction quality crystal of cobalt(III) complex was grown at room temperature (r.t.) by slow evaporation of the complex in dimethylformamide solvent. Intensity data for a dark orange crystal with approximate dimensions $0.3 \times 0.2 \times 0.2$ mm were measured at r.t. 273(2) K on an Enraf–Nonius CAD4 diffractometer using monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) with a scan mode of $\omega$–$2\theta$. No decomposition of the crystal occurred during the data collections. The Co atom was located from an E-map . The other non-hydrogen atoms were determined with successive difference Fourier syntheses. Final refinement by full-matrix least-squares methods was carried out with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms, included in the refinement were located in succeeding difference Fourier synthesis after the non-hydrogen atoms were refined anisotropically.

## 3. Results and discussion

The analytical data of the ligand (Table 1) is consistent with its proposed molecular formula. All the complexes are insoluble in water and methanol, but readily soluble (except copper complex) in $CHCl_3$, DMF and DMSO. The copper complex is sparingly soluble in DMF and DMSO. The physico-chemical and analytical data for all the complexes are given in Table 1. The analytical data (Table 1) are consistent with the proposed molecular formula. The molar conductivity data reveal the nonelectrolytic nature of all the complexes. Cobalt(III) and nickel(II) complexes are diamagnetic and the magnetic moment of the copper(II) complex is found to be 1.24 BM indicating the presence of one unpaired electron. The value is subnormal because it is quite less than the experimental magnetic moment (1.9–2.1 BM) values. It may suggest the existence of polymeric species.

### 3.1. Electronic spectra

The electronic spectra (Table 2) of the cobalt complex are recorded in $CHCl_3$ and DMF. The most intense band in the highest energy region has been assigned to $\pi$–$\pi^*$ transition of ligand. The next lowest energy band found at 27 397 $cm^{-1}$ (in $CHCl_3$), 27 777 $cm^{-1}$ (in DMF) has been assigned to charge transfer transitions [13].

In the electronic spectrum of the nickel complex in DMF, three bands are observed at 10 152 cm − 1 ($\nu_1$); 17 094 ($\nu_2$); 22 772 $cm^{-1}$ ($\nu_3$) assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions [14], respectively. The ratio of $\nu_1$:$\nu_2$ lies at 1.68 as required for an octahedral Ni(II) complex. The ligand field parameters, field splitting energy (10 Dq), Racah interelectronic repulsion parameter $\beta$, covalent factor and ligand field stabilization energy (LFSE) have been calculated and presented in Table 3. The electronic data (in DMF) suggest an octahedral geometry for the nickel

Table 2
Electronic spectral band ($cm^{-1}$) for the metal complexes of BMO

| Complex | $CHCl_3$ | | DMF | |
|---|---|---|---|---|
| | Intraligand and charge transfer | d–d | Intraligand and charge transfer | d–d |
| $[Co(BMO)_3]$ | 33 222<br>27 397 | | 33 222<br>27 777 | |
| $[Ni(BMO)_2]$ | 33 898<br>28 901<br>27 777 | 16 806 | 34 482<br>28 901<br>27 777 | 17 094<br>10 152 |
| $[Cu(BMO)]_n$ | 33 557 | 16 949 | 23 333<br>24 390 | 16 863 |

Table 3
Electronic spectral data and ligand field parameters for the nickel complex

| Method of evaluation | $\nu_1$ ($cm^{-1}$) | $\nu_2$ ($cm^{-1}$) | $\nu_3$ ($cm^{-1}$) | $B$ | $B_{35}$ [b] | $\delta_V$ [a] | 10 Dq | $\nu_2-\nu_1$ | $\nu_2/\nu_1$ | LFSE (K $cal^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| Observed | 10 152 | 17 094 | 27 777 | | | | 10 152 | 6942 | 1.68 | 29.00 |
| Calculated | 10 Dq | 19 702 | 25 168 | 961 | 0.923 | 2607 | 10 152 | 9550 | 1.94 | |

[a] Difference in the observed and calculated value of frequencies.
[b] Ratio of the free ion and the complex.

Table 4
Important IR spectral bands and their assignments

| Ligand/complex | $\nu$(OH) | $\nu$(C=O) | $\nu$(C=N) | $\nu$(N–O) | $\nu_{asy}$(C–$C_6H_5$) | $\nu_{sym}$(C–$C_6H_5$) | $\nu$(M–O) | $\nu$(M–N) |
|---|---|---|---|---|---|---|---|---|
| BMO | 3389 | 1647 | 1597 | 1211 | 1493 | 1373 | – | – |
| $[Co(BMO)_3]$ | – | 1597 | 1576 | 1277 | 1493 | 1377 | 490 | 445 |
| $[Ni(BMO)_2]$ | – | 1589 | 1562 | 1269 | 1446 | 1346 | 459 | 424 |
| $[Cu(BMO)]_n$ | – | 1583 | 1556 | 1271 | 1439 | 1336 | 456 | 422 |

complex. DMF is a known coordinating solvent and presumably coordinates nickel in both axial positions to complete the octahedral structure.

The electronic spectrum of the nickel complex is also recorded in chloroform. The spectral behavior in chloroform is in agreement with the square-planar coordination of nickel. The electronic spectrum of the copper complex is recorded in DMF covering a 50 000–125 000 $cm^{-1}$ range. The absorption band is observed at 33 330 $cm^{-1}$ is due to $\pi-\pi^*$/charge transfer transition. However, the low intensity band is observed at 16 863 $cm^{-1}$. This band is assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$ transition [14,15] suggesting the presence of square-planar geometry.

### 3.2. IR spectra

Important IR spectral bands of BMO and its complexes are given in Table 4. A broad band of medium intensity is observed at 3389 $cm^{-1}$ in the spectrum of the free ligand. This band is absent in the spectra of all complexes suggesting the deprotonation of oxime proton in complex formation. The downward shift of $\nu$(C=N) and $\nu$(C=O) bands in the spectra of all complexes suggests the coordination of the metal ion through the azomethine nitrogen and the oxygen atom of the C=O group. The non ligand bands in the 456–490 and 422–445 $cm^{-1}$ regions are tentatively assigned to $\nu$(M–O) and $\nu$(M–N) stretching vibrations [16], respectively.

### 3.3. $^1H$ NMR spectra

Cobalt(III) and nickel(II) complexes are characterized by high resolution (400 MHz) $^1H$ NMR spectra in $CDCl_3$ solvent. In the case of the ligand a singlet is observed in the low field region of the spectra at $\delta$ 8.227 ppm, but it is absent in the cobalt and nickel complexes, which indicates the absence of an oxime proton in these complexes.

Table 5
Cyclic voltammetric data of cobalt, nickel and copper complexes ($10^{-3}$ M) in DMF containing 0.1 M $TEAClO_4$ at 1.0 $V/S^{-1}$ at glassy carbon electrode (Temp. 26°C)

| Complex | Scan rate | Redox couple | $E_{pc}$ (V) | $E_{pa}$ (V) | DE (mV) | $E_{1/2}$ (V) | $-i_c/i_a$ |
|---|---|---|---|---|---|---|---|
| $[Co(BMO)_3]$ | 100 | III/II | −0.52 | −0.18 | 340 | 0.35 | |
| | | II/I | −0.128 | | | | |
| $[Ni(BMO)_2]$ | 100 | II/I | −1.20 | | | | |
| $[Cu(BMO)]_n$ | 100 | III/II | +0.28 | +0.55 | 270 | 0.415 | 0.651 |

### 3.4. Cyclic voltammetric studies

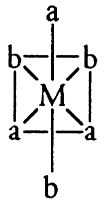
The cyclic voltammograms for cobalt, nickel and copper complexes are recorded in dimethylformamide. The cyclic voltammetric data for all the complexes are given in Table 5.

The cyclic voltammogram of the present cobalt complex has a single reversible electron [Co(III) → Co(II)] couple with $E_{1/2} = -0.35$ V. This complex also has an irreversible cathodic peak at $E_{pc} = -1.28$ V, corresponding to Co(II) → Co(I).

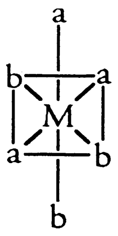
The cyclic voltammogram data for the copper complex show a single reduction wave at $E_{1/2} = +0.415$ V and have a quasi reversible behavior [17] as indicated by the non-equivalent current intensity of cathodic and anodic peaks ($-i_c/i_a = 0.615$ at 100 mV $s^{-1}$). The reversible couple is assigned to Cu(III) → Cu(II), which is similar to values reported earlier [18–21].

Electronic spectral data together with magnetic moment data suggest an octahedral structure of the $[Co(BMO)_3]$ complex. Thus, it is a tris(benzil-α-monoximato)cobalt(III) complex.

No isomers are possible for tris-chelated complexes with symmetrical ligands. However, cobalt complexes with unsymmetrical ligands give facial and meridonial isomers.



facial



meridonial

The present ligand, BMO is unsymmetrical ligand. Now the question is whether the $Co(BMO)_3$ has facial configuration or meridonial configuration. The $^1H$ NMR spectrum of $Co(BMO)_3$ gave no information about the configuration of the complex. Hence it is considered worthwhile to study the complex using the X-ray diffraction technique. The results obtained in the X-ray structure determination of the complex are presented herein.

### 3.5. X-ray crystal and molecular structure of the cobalt(III) complex of BMO

The crystallographic data and data collection details for$[Co(BMO)_3]$ are summarized in Table 6. The molecular structure of $[Co(BMO)_3]$ is shown in Fig. 1 and the important bond lengths and bond angles are listed in Table 7.

From Fig. 1, it can be seen that cobalt is six-coordinate with three nitrogen atoms [N(1), N(2), N(3)] and three oxygen atoms [O(2), O(4), O(6)], thus giving an octahedral configuration from three unsymmetrically bonding bidentate ligands.

As expected, the three imino nitrogen atoms give stronger coordination bonds. This is evident by shorter Co–N bond lengths (1.868–1.901 Å). The Co–O bond

Table 6
Crystal data collection parameter for $[Co(BMO)_3]$

| | |
|---|---|
| Empirical formula | $C_{42}H_{30}CoN_3O_6$ |
| Crystal color | orange |
| Formula weight | 731.62 |
| Temperature (K) | 293(2) |
| $\lambda$ (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P21/c$ |
| $a$ (Å) | 18.165(2) |
| $b$ (Å) | 10.0260(12) |
| $c$ (Å) | 19.962(4) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 98.638(13) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 3594.3(9) |
| $Z$ | 4 |
| $D_{calc}$ (mg $cm^{-3}$) | 1.352 |
| $\mu$(Mo K$\alpha$) ($cm^{-1}$) | 0.530 |
| $F$(000) | 1512 |
| Crystal (dimension mm) | 0.3 × 0.2 × 0.2 |
| Index ranges: $h, k, l$ | −21–21, 0–11, 0–23 |
| Number of reflections collected | 6288 |
| Unique reflections | 6288 |
| Absorption correction | Psi scan |
| Max. and min. transmission | 0.99 and 0.9 |
| Final $R$, $R_w$ | $R_1 = 0.0547$,<br>$wR_2 = 0.1395$ |
| $R$ indices (all data) | $R_1 = 0.0949$,<br>$wR_2 = 0.1534$ |
| Extinction coefficient | 0.0000(4) |
| Largest difference peak and hole (e Å$^{-3}$) | 0.523 and −0.555 |

Table 7
Selected bond lengths (Å) and angles (°) for [Co(BMO)$_3$] with e.s.d values in parentheses [a]

| | |
|---|---|
| Co–N(1) | 1.868(3) |
| Co–N(2) | 1.881(3) |
| Co–N(3) | 1.901(3) |
| Co–O(4) | 1.906(2) |
| Co–O(2) | 1.918(2) |
| Co–O(6) | 1.933(3) |
| O(1)–N(1) | 1.266(4) |
| O(2)–C(8) | 1.279(4) |
| O(3)–N(2) | 1.236(4) |
| O(4)–C(22) | 1.300(4) |
| O(5)–N(3) | 1.275(4) |
| O(6)–C(36) | 1.301(4) |
| N(1)–C(1) | 1.328(4) |
| N(2)–C(15) | 1.364(4) |
| N(3)–C(29) | 1.295(4) |
| C(15)–C(22) | 1.443(5) |
| C(29)–C(36) | 1.434(5) |
| N(1)–Co–N(2) | 94.79(14) |
| N(1)–Co–N(3) | 96.91(12) |
| N(2)–Co–N(3) | 94.48(12) |
| N(1)–Co–O(4) | 177.52(12) |
| N(2)–Co–O(4) | 83.71(11) |
| N(3)–Co–O(4) | 85.19(11) |
| N(1)–Co–O(2) | 82.56(11) |
| N(2)–Co–O(2) | 88.75(12) |
| N(3)–Co–O(2) | 176.76(13) |
| O(4)–Co–O(2) | 95.43(9) |
| N(1)–Co–O(6) | 90.38(13) |
| N(2)–Co–O(6) | 174.27(11) |
| N(3)–Co–O(6) | 82.43(11) |
| O(4)–Co–O(6) | 91.21(10) |
| O(2)–Co–O(6) | 94.38(11) |
| C(8)–O(2)–Co | 112.4(2) |
| C(22)–O(4)–Co | 111.2(2) |
| C(36)–O(6)–Co | 110.9(2) |
| O(1)–N(1)–C(1) | 121.1(3) |
| O(1)–N(1)–Co | 122.8(2) |
| C(1)–N(1)–Co | 116.1(2) |
| O(3)–N(2)–C(15) | 120.5(3) |
| O(3)–N(2)–Co | 123.9(2) |
| C(15)–N(2)–Co | 115.5(3) |
| O(5)–N(3)–C(29) | 123.3(3) |
| O(5)–N(3)–Co | 119.8(2) |
| C(29)–N(3)–Co | 116.5(2) |
| N(1)–C(1)–C(8) | 110.9(3) |
| N(1)–C(1)–C(2) | 119.3(3) |
| O(2)–C(8)–C(1) | 117.7(3) |
| O(2)–C(8)–C(9) | 114.8(3) |
| N(2)–C(15)–C(22) | 109.0(3) |
| N(2)–C(15)–C(16) | 122.1(3) |
| O(4)–C(22)–C(15) | 119.0(3) |
| O(4)–C(22)–C(23) | 115.1(3) |
| N(3)–C(29)–C(36) | 111.0(3) |
| N(3)–C(29)–C(30) | 120.5(3) |
| O(6)–C(36)–C(29) | 118.8(3) |
| O(6)–C(36)–C(37) | 116.4(3) |

[a] Symmetry transformations used to generate equivalent atoms.

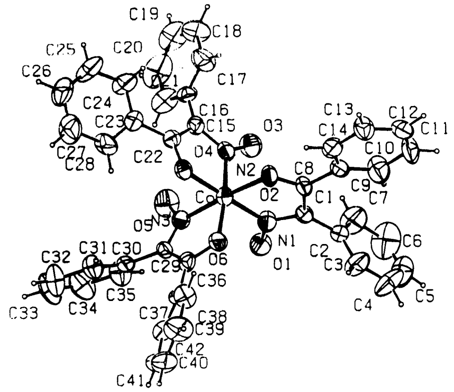


Fig. 1. Molecular structure of [Co(BMO)$_3$] with numbering scheme.

lengths fall in the 1.906–1.933 Å range. The Co–N and Co–O bond lengths are comparable to those of the cobalt(III) complexes containing nitrogen and oxygen donor atoms.

The distances of C(1)–C(8) (1.424 Å), C(15)–C(22) (1.443 Å) and C(29)–C(36) (1.434 Å) are shorter than the normal C–C single bond and larger than the C=C, suggesting the delocalization of electrons in the complexed ligand systems.

The ligand acts as an uninegative unsymmetrical bidentate ligand. The oxime hydrogen is absent in the structure. The ligands are arranged in facial configuration at the metal center.

## 4. Supplementary material

Supplementary data are available on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) by quoting the deposition number CCDC 138847.

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