Research Article

Use of the 2-Pyridinealdoxime/N,N′-Donor Ligand Combination in Cobalt(III) Chemistry: Synthesis and Characterization of Two Cationic Mononuclear Cobalt(III) Complexes

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The use of 2-pyridinealdoxime (paoH)/N,N′-donor ligand (L-L) “blend” in cobalt chemistry has afforded two cationic mononuclear cobalt(III) complexes of the general type [Co(pao)2(L-L)]+, where L-L = 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy). The CoCl2/paoH/L-L (1 : 2 : 1) reaction system in MeOH gives complexes [CoIII(pao)2(phen)]Cl·2H2O (1·2H2O) and [CoIII(pao)2(bpy)]Cl·1.5MeOH (2·1.5MeOH). The structures of the complexes were determined by single-crystal X-ray crystallography. The Co III ions are six-coordinate, surrounded by three bidentate chelating ligands, that is, two pao− and one phen or bpy. The deprotonated oxygen atom of the pao− ligand remains uncoordinated and participates in hydrogen bonding with the solvate molecules. IR data of the complexes are discussed in terms of the nature of bonding and the known structures.

1. Introduction

Oximes and their metal complexes are of current interest because of their rich physicochemical properties, reactivity patterns, and potential applications in many important chemical processes in the fields of medicine [1, 2], bioorganic chemistry [3], catalysis [4], and electrochemical and electrooptical sensors [5].

In the treatment of organophosphate insecticide toxicity in man and animals, the use of acetylcholinesterase reactivators in conjunction with atropine has been found to be the most effective treatment [6]. Among various acetylcholinesterase reactivators, 2-pyridinealdoxime (paoH) is routinely used in human and veterinary practices. It is furthermore known that metal complexes of active drugs as ligands can have important pharmaceutical activities because of several factors. In fact, the field of medicinal inorganic chemistry emerged a long time ago [7], and it is based on certain principles that can be summarized as follows. Complexation with the metal protects the drug against enzymatic degradations because of the inertness of certain metal-ligand linkages. The metal complex can have better hydrophobicity/hydrophilicity properties than the free ligand and, through this, it can improve the transport processes in the tissues. In addition, the metal complex can release the active drug(s) in a specific organ, and its activity can be reinforced by the combination of effects from the ligands and from the metal residue. The application of these principles has already resulted in the design of successful metal-based drugs [8, 9].

Since 1905, when Tschugaeff introduced dimethylglyoxime as a reagent for the analysis of nickel, oxime ligands have played an important role in the continuing progress of coordination chemistry [10]. Furthermore, the ability of the oximate(-1) group (>C=N–O−) to stabilize oxidized forms of metal ions, for example, NiIII or NiIV, has a vital importance in their role in the areas of technological applications [11]. In contrast to the great number of studies dealing with
metal complexes of simple oximes and salicylaldoximes [12],
relatively little is known about complexes of 2-pyridyloximes
[13–15] although this class of compounds could offer unique
features in terms of structural and physical properties.

Few years ago our group explored the influence of
these ligands on the Co cluster chemistry by reacting cobalt
carboxylate salts with neutral 2-pyridyloximes; the main
objectives were the access to new structural types of clusters
with interesting magnetic and spectroscopic properties and
the study of Co-mediated reactions of the oxime group.
Reaction schemes involving di-2-pyridyl ketone oxime, dpkoxH
(Figure 1), and various Co carboxylate sources led [16] to
the first mixed-valence Co(II,III), inverse 12-metallacrown-4
complexes, namely, [CoII2CoIII(OR)2(O2CR′)2(dpkox)4S2]X2
(R = H, CH3; R′ = CH3, C6H5, (CH3)3; S = solvent; X = ClO4, PF6). The use of phenyl 2-pyridyl ketone
oxime, phpkoxH (Figure 1), methyl 2-pyridyl ketone
oxime, MepaoH (Figure 1), and 2-pyridinealdoxime,
paoH (Figure 1) in Co carboxylate chemistry yielded [17]
the trinuclear, mixed-valence, carboxylate-free Co(II,III)
complexes [Co3(phpkox)6](PF6)2, [Co3(Mepao)6](ClO4)2,
and [Co3(pao)6](ClO4)2. The core of these complexes has
an open-topology comprising one CoII center and two CoIII
ions. Recently [18] two of us reported complexes [CoIII3O(O2CPh)3(pao)3][CoII5(O2CPh)8]2,[CoIII3O(O2CPh)3(pao)3][O2CPh],
[CoIII3O(O2CPh)3(pao)3][O2CPh](NO3), and [CoIII2CoII(OH)Cl3(pao)4]. The above prior results
encouraged us to proceed to the amalgamation of 2-
pyridyl oximes with N,N′-donor ligands, that is, 1,10-
phenanthroline (phen) and 2,2′-bipyridine (bpy) (Figure
1), in cobalt chemistry. The primary aim of this project was
the synthesis and structural characterization of a series of
cobalt building blocks that could act as “metalloligands”
for the construction of one-dimensional heterometallic
assemblies with various transition metal ions (e.g., MnIII,
CrIII, FeII) or lanthanides; the latter chains would probably
provide interesting magnetic, optical, and spectroscopic
properties. A secondary goal was the study of the biological
properties of the resulting mixed-ligand complexes.

Herein, we concentrate on the synthetic investigation of
the general CoCl2/paoH/phen or bpy reaction system
and describe the preparation and characterization of the
cationic mononuclear complexes [Co(pao)2(phen)]Cl and
[Co(pao)2(bpy)]Cl.

2. Experiments

2.1. Starting Materials and Physical Measurements. All
manipulations were performed under aerobic conditions
using reagents and solvents as received. Cobalt(II) chloride,
2-pyridinealdoxime (paoH), 1,10-phenanthroline hydrate
(phen·H2O), and 2,2′-bipyridine (bpy) were purchased from
Aldrich Co. Elemental analyses (C, H, N) were performed by
the University of Ioannina (Greece) Microanalytical Labora-
tory using an EA 1108 Carlo Erba analyzer. Ir spectra (4000–
450 cm−1) were recorded on a Perkin-Elmer 16 PC FT-IR
spectrometer with samples prepared as KBr pellets. Solid-
state (diffuse reflectance, 28.5–12.5 kK) electronic spectra
were recorder on a Varian Cary 100 instrument. Magnetic
susceptibility measurements were carried out at 25°C by
the Faraday method using a Cahn-Ventron RM-2 balance
standardized with [HgCo(NCS)4]n.

2.2. Compound Preparation

2.2.1. Preparation of [Co(pao)2(phen)]Cl-2H2O (1-2H2O).
To a pale yellow, stirred solution of paoH (0.12 g, 1.0 mmol)
in MeOH (20 cm3) was added a colourless solution of
phen·H2O (0.10 g, 0.5 mmol) in the same solvent (5 cm3).
To the resulting, almost colourless solution, a pink solution
of CoCl2 (0.07 g, 0.5 mmol) in MeOH (10 cm3)w a sa d d e d .
The deep orange solution obtained was stirred at ambient
temperature for 30 min and allowed to very slowly evaporate
at 6–8°C for one week. Well-formed, X-ray quality crystals of
the product slowly appeared. The orange prismatic crystals
were collected by filtration, washed with cold MeOH (2 ×
3 cm3) and Et2O (2 × 4 cm3), and dried in air. Yields as
high as 70% were obtained (found: C, 51.9; H, 3.8; N, 15.6.
C24H22CoN6O4Cl calcd.: C, 52.1; H, 4.0; N, 15.2%).
2.2. Preparation of \([\text{Co(pao)}_2(\text{bpy})]\)Cl-1.5MeOH (2.1.5MeOH). To a pink, stirred solution of CoCl\(_2\) (0.07 g, 0.5 mmol) in MeOH (15 cm\(^3\)) was added solid paoH (0.12 g, 1.0 mmol). To the resulting deep orange solution a colourless solution of bpy (0.08 g, 0.5 mmol) in the same solvent (5 cm\(^3\)) was added. The solution was stirred at ambient temperature for 25 min, filtered, and the filtrate was layered with Et\(_2\)O/n-hexane (40 cm\(^3\), 1:1 v/v). Slow mixing gave well-formed, X-ray quality crystals of the product. The reddish orange prismatic crystals were collected by filtration, washed with cold MeOH (2 × 3 cm\(^3\)) and Et\(_2\)O (2 × 3 cm\(^3\)), and dried in air. Yields as high as 75% were obtained. The crystals were found to lose solvent readily; the dried sample analysed for [Co(pao)]\(_2\)(bpy)Cl, that is, 2 (found: C, 53.3; H, 3.4; N, 17.2. C\(_{22}\)H\(_{18}\)CoN\(_6\)O\(_3\)Cl calcld.: C, 53.6; H, 3.7; N, 17.1%).

2.3. X-Ray Crystallographic Studies \([1]\). Suitable crystals of 1\(\cdot\)2H\(_2\)O were sealed in capillary filled with drops of the mother liquor, while crystals of 2\(\cdot\)1.5MeOH were mounted in air and covered with epoxy glu. Diffraction measurements of 1\(\cdot\)2H\(_2\)O and 2\(\cdot\)1.5MeOH were made on a Crystal Logic dual goniometer diffractometer using graphite-monochromated Mo radiation. Crystal data and full details of the data collection and data processing are listed in Table 1. Unit cell dimensions were determined and refined by using three angular settings of 2\(\theta\) automatically centred reflections in the range 11\(\degree\) < \(\theta\) < 23\(\degree\) for both complexes. Three standard reflections, monitored every 97 reflections, showed less than 3% intensity variation and no decay. Lorentz-polarisation corrections were applied for both complexes.

### Table 1: Crystallographic data for complexes 1\(\cdot\)2H\(_2\)O and 2\(\cdot\)1.5MeOH.

| Parameter | 1\(\cdot\)2H\(_2\)O | 2\(\cdot\)1.5MeOH |
|-----------|----------------|-----------------|
| Color (habit) | Red/orange prisms | Red prisms |
| Crystal size (mm) | 0.33 × 0.08 × 0.05 | 0.50 × 0.35 × 0.30 |
| Chemical formula | C\(_{22}\)H\(_{22}\)CoN\(_6\)O\(_4\)Cl | C\(_{23}\)H\(_{29}\)CoN\(_6\)O\(_3\)Cl |
| \(M\) | 552.86 | 535.83 |
| Crystal system | Tetragonal | Orthorhombic |
| Space group | \(I_4_1acd\) | \(Ic2m\) |
| Unit cell dimensions | | |
| \(a\) (Å) | 17.098(5) | 13.134(6) |
| \(b\) (Å) | 17.098(5) | 8.900(4) |
| \(c\) (Å) | 31.903(9) | 21.293(8) |
| \(V\) (Å\(^3\)) | 9327(5) | 2489(2) |
| \(Z\) | 16 | 4 |
| \(D_{alc}\) (g cm\(^{-3}\)) | 1.575 | 1.430 |
| \(\mu\) (mm\(^-1\)) | 0.896 | 0.836 |
| Radiation (Å) | MoK\(_a\) (0.71073) | MoK\(_a\) (0.71073) |
| Temperature (K) | 298 | 298 |
| Scan mode/speed (° min\(^{-1}\)) | \(\theta\)-20/2.6 | \(\theta\)-2θ/3.5 |
| Scan range (°) | 2.1 + \(\alpha_1\)\(\alpha_2\) separation | 2.3 + \(\alpha_1\)\(\alpha_2\) separation |
| \(\theta\) range (°) | 2.1–23.0 | 1.8–25.0 |
| Reflections collected | 3157 | 3561 |
| Reflections used \([I > 2\sigma(I)]\) | 1627 \((R_{int} = 0.0276)\) | 2253 \((R_{int} = 0.0240)\) |
| Parameters refined | 164 | 204 |
| \(|\Delta\sigma/\sigma|_{\text{max}}\) | 0.000 | 0.014 |
| \(|\Delta\rho|_{\text{max}}/|\Delta\rho|_{\text{min}}\) (e Å\(^{-3}\)) | 0.712/–0.444 | 0.695/–0.244 |
| GoF (on \(F^2\)) | 1.101 | 1.079 |
| \(R_1^{(a)}\) \([I > 2\sigma(I)]\) | 0.0543 | 0.0424 |
| \(wR_2^{(b)}\) \([I > 2\sigma(I)]\) | 0.1453 | 0.1097 |

\((a) R_1 = \Sigma(|F_o| - |F_o|)/\Sigma(|F_o|); \ (b) wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}, \ w = 1/[(\alpha_1^2(F_o^2) + (a\sigma)^2 + b\beta)] where P = (max(F_o^2, 0) + 2F_c^2)/3.\)
Addition of one equivalent of LiOH \cdot H_2O in the above described reaction mixtures leads to complexes 1 \cdot 2H_2O and 2 \cdot 1.5MeOH as well as to unidentified noncrystalline, hydroxo compounds. (b) A number of attempts were made for the isolation of new products by increasing or decreasing the paoH/Co reaction ratio, keeping constant (1 : 1) the phen or bpy : Co ratio. Increasing the former ratio, that is, to 3 : 1 or 4 : 1, complexes 1 and 2 remained the main products; however, these were contaminated with variable amounts of the known product [Co^{III} (pao)_{3}] [21] (analytical evidence, unit cell determination of the isolated dark orange crystals). Reducing the above reaction ratio (1 : 1 and/or 0.5/1), paoH—“free” products were isolated containing only bpy or phen and chloride ions. We have not yet found evidence for the existence of the mixed-ligand species [Co(pao)(phen)]Cl_2 and [Co(pao)(bpy)]_2Cl_2. (c) Both complexes are soluble in water, dimethylformamide, dimethylsulfoxide, and acetonitrile, less soluble in nitromethane and ethanol, and insoluble in benzene, chloroform and dichloromethane.

3.2. Description of Structures. Labeled ORTEP plots of complexes 1 \cdot 2H_2O and 2 \cdot 1.5MeOH are shown in Figures 2 and 4, respectively. Selected bond distances and angles for complexes 1 \cdot 2H_2O and 2 \cdot 1.5MeOH are listed in Table 2.

Disregarding the different nature of the N,N’-donor ligands, compounds 1 \cdot 2H_2O and 2 \cdot 1.5MeOH display strikingly similar molecular structures. Thus, only the structure of the former will be described in detail.

Complex 1 \cdot 2H_2O crystallizes in the tetragonal space group I\_41/acd. Its structure consists of the mononuclear [Co(pao)_{2}(phen)]Cl \cdot 2H_2O (1 \cdot 2H_2O). Following a similar reaction scheme and replacing only the corresponding bidentate ligand with 2,2’-bipyridine (bpy), we were able to obtain red crystals suitable for crystallography. The new product was identified as [Co(pao)(bpy)]Cl \cdot 1.5MeOH (2 \cdot 1.5MeOH).

The most noticeable feature of this reaction scheme is the deprotonation of the oximato group without the existence of a strong base in the reaction system. Reduction products of the atmospheric oxygen, which is responsible for Co^{II} \rightarrow Co^{III} oxidation, are possible agents for the former deprotonation. The formation of 1 and 2 can be summarized by the stoichiometric equations (1) and (2), respectively,

\[
\begin{align*}
2\text{CoCl}_2 + 4\text{paoH} + 2\text{phen} \cdot H_2O + 1/2 \text{O}_2 & \xrightarrow{\text{MeOH}} 2[\text{Co(pao)}_{2}(\text{phen})]\text{Cl} + 2\text{HCl} + 3\text{H}_2\text{O} \quad (1) \\
2\text{CoCl}_2 + 4\text{paoH} + 2\text{bpy} + 1/2 \text{O}_2 & \xrightarrow{\text{MeOH}} 2[\text{Co(pao)}_{2}(\text{bpy})]\text{Cl} + 2\text{HCl} + \text{H}_2\text{O} \quad (2)
\end{align*}
\]

The following experimental points should be mentioned at this point. (a) The reactions between CoCl_2, paoH and N,N’-donor ligands in MeOH are [OH^-]-independent.
Table 2: Selected bond distances (Å) and angles (°) for complexes 1·2H₂O and 2·1.5MeOH, with the estimated standard deviations in parentheses.

| Bond distances                  | 1·2H₂O     | 2·1.5MeOH  |
|--------------------------------|------------|------------|
| Co–N(1)                        | 1.928(4)   | 1.937(3)   |
| Co–N(2)                        | 1.904(4)   | 1.909(4)   |
| Co–N(3)                        | 1.986(4)   | 1.977(4)   |
| Co–N(1’)                       | 1.928(4)   | 1.937(3)   |
| Co–N(2’)                       | 1.904(4)   | 1.909(4)   |
| Co–N(3’)                       | 1.986(4)   | 1.977(4)   |
| N(2)–O/O(1)                    | 1.294(6)   | 1.273(5)   |
| N(3)–C(7)                      | 1.322(7)   | 1.343(6)   |
| N(1)–C(1)                      | 1.343(7)   | 1.340(6)   |
| N(2)–C(6)                      | 1.298(7)   | 1.309(7)   |

| Bond angles                    |            |            |
|--------------------------------|------------|------------|
| N(3)–Co–N(3’)                  | 82.7(2)    | 82.2(2)    |
| N(1)–Co–N(3)                   | 88.6(2)    | 93.6(2)    |
| N(1)–Co–N(2)                   | 83.7(2)    | 83.7(2)    |
| N(2)–Co–N(2’)                  | 89.9(3)    | 89.8(2)    |
| N(1)–Co–N(3’)                  | 96.1(2)    | 90.7(2)    |
| Co–N(2)–O/O(1)                 | 122.7(4)   | 123.3(3)   |

*Unprimed and primed atoms are related by symmetry.

Since the space group of 1·2H₂O is centrosymmetric and the space group of 2·1.5MeOH involves a mirror plane, both complexes are racemic mixtures of their Δ and Λ enantiomorphs.

Complexes 1 and 2 join a small family of structurally characterized homo- [17, 18, 21] and heterometallic [22, 23] Co complexes featuring pao⁻ as ligand. Many years ago Blackmore and Magee [24, 25] and Grant and Magee [26] studied the reactions between 2-pyridinealdoxime and various CoII sources under a variety of reaction conditions. Structural assignments of the solid products [24, 26] were based on spectroscopic data; no X-ray structures were reported. The authors did not prepare mixed-ligand complexes.

3.3. Physical and Spectroscopic Characterization. Complexes 1 and 2 are diamagnetic, in accordance with their low-spin 3d⁶ character.
TABLE 3: Hydrogen bonding interactions in 1·2H2O.

| Interaction D–H···A | D···A (Å) | H···A (Å) | D–H···A (°) | Symmetry operation of A |
|-------------------|----------|----------|------------|------------------------|
| OW-HWA···O        | 2.854(7) | 1.740(4) | 161.7(3)   | x, y, z                |
| OW-HWB···Cl       | 3.124(6) | 1.978(2) | 163.5(3)   | x, y, z                |

Figure 5: Packing diagram of complex 2·1.5MeOH along the c axis. The metal coordination spheres are polyhedron designed (purple). The chloride counteranions and the methanol solvate molecules have been omitted.

The solid-state (diffuse reflectance) UV-Vis spectra of the two complexes are almost identical and typical for low-spin CoIII-N6 chromophores [27]. The low-spin octahedral ground term is 1A1g, and there are two relatively low lying spin allowed transitions, with lower lying spin triplet partners, all derived from (t2g)2(eg). Under this scheme, the bands in the spectra of 1 and 2 at ∼29.0, 21.5, 17.0, and 13.5 kK are assigned [27] to the 1A1g → 1T2g, 1T1g, 3T2g, and 3T1g transitions, respectively, although a superposition of the highest energy d-d transition and a charge transfer band should not be ruled out.

Two bands, one of medium intensity at ∼1015 cm−1 assigned to ν(N–O) and one strong at 1599 cm−1 assigned to ν(C=N)_{aximale} are common in the IR spectra of the two complexes [21]; the higher-wavenumber band most probably overlaps with an aromatic stretch. The in-plane deformation of the 2-pyridyl ring of the free paoH at 627 cm−1 shifts upward on coordination in the spectra of 1 (643 cm−1) and 2 (645 cm−1) [28].

4. Conclusions

The present work extends the body of results that emphasizes the ability of the monoanionic ligand pao− to form interesting structural types in 3d metal chemistry. The use of both paoH and phen or bpy in reactions with CoII sources has led to products 1 and 2, the first mixed-ligand CoIII noncarboxylate complexes involving paoH/pao−. Of interest is the nonparticipation of the deprotonated oximate oxygen atom in coordination; this is due to the involvement of the negatively charged oxygen in hydrogen bonding.

Complexes of trivalent 3d metals (e.g., CrIII, MnIII, FeIII) other than CoIII with the pao−/phen or bpy ligand combinations are not known to date, and it is currently not evident whether the structures of such compounds are dependent on the particular nature of the metal ion. We are studying this matter. Synthetic efforts are also in progress to use 1 and 2 as “metalloligands” for the preparation of heterometallic CoIII/MII complexes (M = Fe, Mn, lanthanides).

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