Synthesis, Crystal Structure and Thermodynamic Properties of 
Tris(8-Quinolinolato-N,O)cobalt(III) Methanol

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8-Hydroxyquinoline has been used in large-scale industrial application. For example, some intermediate products of dyestuffs and drugs were prepared using 8-hydroxyquinoline. In addition, some 8-hydroxyquinoline metal complexes have been used as organic electroluminescent devices. For example, tris(8-hydroxyquinolinolato)aluminium(III) is an important part of organic light-emitting devices (OLEDs) due to its advantages in quantum efficiency, carrier mobility and thermal stability. Among this research a variety of 8-hydroxyquinoline metal coordination compounds have been explored for the design of OLEDs\(^1\). The present cobalt(III) compound may be a kind of potential light-emitting material.

Li et al.\(^2\) synthesized the present compound and investigated its crystal structure. However, lattice energy and some important thermodynamic properties of the present compound have not been found in the literature, which restricted the progress of relevant theoretical studies and application development of the compounds used as the light-emitting material. Lattice energy has an important role in evaluating the stability of new materials. Heat capacity is one of the most fundamental thermodynamic properties and closely related to other physical, biological, physiological and chemical properties\(^3,4\). The purpose of the present work is to measure low temperature heat capacities of the compound by an adiabatic calorimeter and thermodynamic functions of the title compound were derived from these experimental results.

EXPERIMENTAL

Cobalt acetate and 8-hydroxyquinoline used as the reactants were of analytical grade with a labeled mass percent purity of 99.5 %. The reactants were accurately weighed at the molar ratio of \([\text{Co(CH}_3\text{COO}_2]:\text{8H}_2\text{NO}] = 1:3\). A solution of 8-hydroxyquinoline (6.6559 g, 0.045 mol) in methanol and another solution of \(\text{Co(CH}_3\text{COO}_2]:\text{4H}_2\text{O}(3.8064 g, 0.015 mol) in the certain amount of methanol were mixed together in a flask of 250 mL. The solution was heated and stirred under reflux for 10 h. The final solution was naturally cooled to room temperature, filtered and the crude product was washed three times by anhydrous methanol. The solid product was recrystallized using anhydrous methanol and brown crystals were obtained. Finally, the sample was placed in a vacuum desiccator to dry for 6 h at 303 K. Theoretical contents of Co, C, H and N in the compound have been calculated as, 11.24, 64.25, 4.21 and 8.05 %, respectively. Chemical analysis and elemental analysis (model: PE-2400, Perkin Elmer, USA) have shown that the practical contents of Co, C, H and N in the compound have been measured to be 11.24, 64.25, 4.21 and 8.03 %, respectively. Chemical analysis and elemental analysis (model: PE-2400, Perkin Elmer, USA) have shown that the practical contents of Co, C, H and N in the compound have been measured to be 11.24, 64.25, 4.21 and 8.05 %, respectively. This showed the mass per cent purity of the sample prepared was higher than 99.50 %. The content of cobalt in the sample was measured by Na\(_2\)EDTA complex titration. It was demonstrated from results of chemical and elemental analysis that one solvent molecule CH\(_3\)OH exists in the coordination compound.
A single crystal with dimensions of 0.33 mm × 0.21 mm × 0.19 mm suitable for X-ray analysis was mounted on a fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD-detector diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by direct methods and expanded using Fourier techniques with the SHELXL-97 program and refined with a full-matrix least-squares technique on F². All non-hydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. Absorption corrections were applied by SADABS. Crystal data and refinement details are summarized in Table-1. Crystal data and structure refinement details are summarized in Table-1.

### Table-1

<table>
<thead>
<tr>
<th>Crystallographic data</th>
<th>Structure refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₉H₈N₂O₅Co</td>
</tr>
<tr>
<td>Formula weight</td>
<td>523.42</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(Å)</td>
</tr>
<tr>
<td>a = 10.8759(12)</td>
<td></td>
</tr>
<tr>
<td>b = 13.1334</td>
<td></td>
</tr>
<tr>
<td>c = 16.700(2)</td>
<td></td>
</tr>
<tr>
<td>α = 90°, β = 97.7310(10°), γ = 90°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>2363.6(5) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.471 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.767 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1080</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.33 mm × 0.21 mm × 0.19 mm</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>1.98-25.02°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-6 ≤ h ≤ 12, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>11705/4156 [R(int) = 0.0358]</td>
</tr>
<tr>
<td>Completeness to θ = 25.02°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4156/1/326</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.000</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0407, wR₁ = 0.0837</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0738, wR₁ = 0.1052</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.406 and -0.361 eÅ⁻³</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Crystal structure:** The molecular structure of Co(C₉H₈N₂O₅)·CH₃OH(s) is shown in Fig. 1. The selected bond lengths and angles of the compound are listed in Table-2. Hydrogen bonds are listed in Table-3. Unit cell parameters are a = 10.8759(12) Å, b = 13.1334 (14) Å, c = 16.700(2) Å, α = 90°, β = 97.7310 (10°) and γ = 90°, respectively. It was found that the crystal system of the coordination compound is monoclinic and the space group is P2₁/n, as shown in Table-1. Three 8-quinolinolinate monoamines chelate to the cobalt atom with an octahedral coordination geometry. The packing of the

![Fig. 1. Structure of the title compound Co(C₉H₈N₂O₅)·CH₃OH(s)](image)
and the structure of the title compound determined was between the neighboring complex molecules. The crystal data almost consistent with the previously reported results by the following formula:

\[ \text{Lattice energy: } U = \gamma \left( \frac{\rho_m}{M_m} \right)^{1/3} + \delta \]  

where \( M_m / g \) (or \( M_g \)) is the chemical formula mass of the ionic material; \( \rho_m / g \text{ cm}^{-3} \) (or \( \rho_g \text{ cm}^{-3} \)) is the density of the substance; coefficients \( \gamma \) and \( \delta \) take the following values for \( M_m, X_m \), (q:p):

\[ \gamma = 2342.6 \text{ I kJ mol}^{-1}, \delta = 55.2 \text{ I KJ mol}^{-1} \]

The quinoline plane containing atom \( N_3 \) parallels to another quinoline plane containing atom \( N(1) \) and the C(1) plane containing \( \alpha \) and \( \beta \) take the following values for \( M_m \):

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Co(1)-O(2)</th>
<th>O(2)-Co(1)-O(1)</th>
<th>Co(1)-N(3)</th>
<th>O(1)-Co(1)-N(3)</th>
<th>Co(1)-N(2)</th>
<th>O(2)-Co(1)-N(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.896(2)</td>
<td>89.64(10)</td>
<td>1.922(3)</td>
<td>93.04(11)</td>
<td>1.905(2)</td>
<td>85.66(11)</td>
</tr>
<tr>
<td></td>
<td>1.935(3)</td>
<td>92.46(10)</td>
<td>1.889(2)</td>
<td>85.70(11)</td>
<td>1.928(3)</td>
<td>92.22(11)</td>
</tr>
<tr>
<td></td>
<td>1.320(4)</td>
<td>91.69(10)</td>
<td>1.372(4)</td>
<td>94.25(11)</td>
<td>1.332(4)</td>
<td>110.62(2)</td>
</tr>
<tr>
<td></td>
<td>1.339(5)</td>
<td>109.52(2)</td>
<td>1.318(4)</td>
<td>110.72(2)</td>
<td>1.367(4)</td>
<td>111.3(2)</td>
</tr>
<tr>
<td></td>
<td>1.328(4)</td>
<td>86.27(11)</td>
<td>1.372(4)</td>
<td>172.47(12)</td>
<td>1.320(4)</td>
<td>130.4(2)</td>
</tr>
<tr>
<td></td>
<td>1.320(4)</td>
<td>131.2(2)</td>
<td>0.8200</td>
<td>129.3(3)</td>
<td>0.9300</td>
<td>111.3(2)</td>
</tr>
<tr>
<td></td>
<td>1.406(5)</td>
<td>121.5(3)</td>
<td>0.9300</td>
<td>119.2</td>
<td>1.405(5)</td>
<td>124.3(3)</td>
</tr>
<tr>
<td></td>
<td>1.375(5)</td>
<td>117.1(3)</td>
<td>1.366(5)</td>
<td>123.0(3)</td>
<td>1.345(5)</td>
<td>114.7(3)</td>
</tr>
<tr>
<td></td>
<td>1.366(5)</td>
<td>114.7(3)</td>
<td>0.9600</td>
<td>123.0(3)</td>
<td>0.9600</td>
<td>123.0(4)</td>
</tr>
</tbody>
</table>

The crystal data consist of the lattice energy (U_{Pot}) is calculated by the following formula:

\[ U_{Pot} = \gamma \left( \frac{\rho_m}{M_m} \right)^{1/3} + \delta \]  

The experimental molar heat capacities of the coordination compound are listed in Table-4 and plotted in Fig. 3, which showed that the heat capacity curve of the compound smoothly increased with temperature. The present compound was thermally stable over the temperature range between \( T = 78 \) and \( 370 \) K, no phase change, association and thermal decomposition occurred. The experimental points in the temperature region between \( T = 78 \) and \( 370 \) K were fitted by the least square method and a polynomial equation of the experimental molar heat capacities (\( C_p,m \)) versus reduced temperature (\( \chi \), \( \chi = f(T) \), have been obtained by eqn. 2:

\[ C_p,m = \frac{1}{2} \left( q_p + q_p' \right) \]  

where \( q_p = \frac{\rho_m}{M_m} \) is the density of the compound; \( \gamma \) and \( \delta \) take the following values for \( M_m, X_m \), (q:p):

\[ \gamma = 2342.6 \text{ I kJ mol}^{-1}, \delta = 55.2 \text{ I KJ mol}^{-1} \]

The lattice energy of the complex is calculated to be 2314.72 kJ mol\(^{-1}\), which reveals that its structure is very stable.

**Low-temperature heat capacities:** The experimental molar heat capacities of the coordination compound are listed in Table-4 and plotted in Fig. 3, which showed that the heat capacity curve of the compound smoothly increased with temperature. The present compound was thermally stable over the temperature range between \( T = 78 \) and \( 370 \) K, no phase change, association and thermal decomposition occurred. The experimental data in the temperature region between \( T = 78 \) and \( 370 \) K were fitted by the least square method and a polynomial equation of the experimental molar heat capacities (\( C_p,m \)) versus reduced temperature (\( \chi \), \( \chi = f(T) \), have been obtained by eqn. 2:

\[ C_p,m = \frac{1}{2} \left( q_p + q_p' \right) \]  

where \( q_p = \frac{\rho_m}{M_m} \) is the density of the compound; \( \gamma \) and \( \delta \) take the following values for \( M_m, X_m \), (q:p):

\[ \gamma = 2342.6 \text{ I kJ mol}^{-1}, \delta = 55.2 \text{ I KJ mol}^{-1} \]  

The lattice energy (U_{Pot}) is calculated by the following formula:

\[ U_{Pot} = \gamma \left( \frac{\rho_m}{M_m} \right)^{1/3} + \delta \]  

where \( M_m / g \) (or \( M_g \)) is the chemical formula mass of the ionic material; \( \rho_m / g \text{ cm}^{-3} \) (or \( \rho_g \text{ cm}^{-3} \)) is the density of the substance; coefficients \( \gamma \) and \( \delta \) take the following values for \( M_m, X_m \), (q:p):

\[ \gamma = 2342.6 \text{ I kJ mol}^{-1}, \delta = 55.2 \text{ I KJ mol}^{-1} \]  

The crystal data consist of the lattice energy (U_{Pot}) is calculated by the following formula:

\[ U_{Pot} = \gamma \left( \frac{\rho_m}{M_m} \right)^{1/3} + \delta \]  

The experimental molar heat capacities of the coordination compound are listed in Table-4 and plotted in Fig. 3, which showed that the heat capacity curve of the compound smoothly increased with temperature. The present compound was thermally stable over the temperature range between \( T = 78 \) and \( 370 \) K, no phase change, association and thermal decomposition occurred. The experimental points in the temperature region between \( T = 78 \) and \( 370 \) K were fitted by the least square method and a polynomial equation of the experimental molar heat capacities (\( C_p,m \)) versus reduced temperature (\( \chi \), \( \chi = f(T) \), have been obtained by eqn. 2:
C_{p,m}(J K^{-1} mol^{-1}) = 406.669 + 58.949X - 10.757 X^2 - 6.900X^{-1} + 6.701 X^{-2}

in which X = (T(K) - 224)/146. The correlation coefficient for the fitting R^2 equaled 0.99999. The value, 224, is half of the upper limit 370 K plus the lower limit 78 K in the temperature range of (78-370) K. While, 146 is half of the upper limit 370 K minus the lower limit 78 K in the same range. The reduced temperature (T) obtained using the method are between -1 and 1 and relative deviations of the smooth heat capacities from the experimental values will become smaller and smaller with the increase of the power of X in the fitted polynomial equation according to the principle in statistics.

The eqn. 2 is valid in the temperature range of (78-370) K. The relative deviations of the smoothed heat capacities obtained by the above equation from experimental heat capacities were within ±0.30 %, as shown in Fig. 4.

Thermodynamic functions of the compound: The smoothed molar heat capacities and thermodynamic functions of the sample were calculated based on the fitted polynomial of the heat capacity as a function of the reduced temperature (X) according to the following thermodynamic equations,

\[
H(T) - H_{(298.15K)} = \int_{298.15K}^{T} C_{p,m}dT
\]

\[
S(T) - S_{(298.15K)} = \int_{298.15K}^{T} C_{p,m}T^{-1}dT
\]
Fig. 4. Plot of the relative deviations, SD (%) = [(C_{smo} – C_{exp})/C_{exp}] × 100 %, of the smoothed molar heat capacities of the compound from the experimental values against the absolute temperature. In which C_{smo} and C_{exp} represent the smoothed and experimental molar heat capacities of the compound.

\[ G(T) - G_{(298.15\text{K})} = \int_{298.15\text{K}}^{T} C_{p,m}dT - T\int_{298.15\text{K}}^{T} C_{p,m}^{-1}dT \] (5)

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated in Table-5 at intervals of 5 K.

Conclusion

The crystal structure, lattice energy, low-temperature heat capacities and some basic thermodynamic functions of tris(8-quinolinolato-N,O)cobalt(III) methanol solvate, were reported. These results are instructive to the applications of 8-hydroxyquinoline metal coordination compounds.

ACKNOWLEDGEMENTS

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REFERENCES