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### Zn(II), Cd(II) and Hg(II) complexes with 2,2'-Biquinoline, syntheses and X-ray crystal structures of [Hg(bq)(SCN)<sub>2</sub>]

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## Zn(II), Cd(II) AND Hg(II) COMPLEXES WITH 2,2'-BIQUINOLINE, SYNTHESSES AND X-RAY CRYSTAL STRUCTURES OF [Hg(bq)(SCN)<sub>2</sub>]

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Reaction of the ligand 2,2'-biquinoline (bq) with Zn(ClO<sub>4</sub>)<sub>2</sub>, CdCl<sub>2</sub> and Hg(SCN)<sub>2</sub> gives complexes [Zn(bq)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Cd(bq)<sub>2</sub>Cl<sub>2</sub>] and [Hg(bq)(SCN)<sub>2</sub>] which were characterized by elemental analyses and IR spectroscopy. The crystal structure of [Hg(bq)(SCN)<sub>2</sub>] was determined by X-ray crystallography. The complex comprises a monomeric Hg(SCN)<sub>2</sub> unit with one 2,2'-biquinoline (bq) ligand coordinated to the Hg atom via the two quinolinic nitrogens, giving rise to a five-membered chelate ring in a distorted tetrahedral environment. A π–π stacking interaction exists between the parallel aromatic rings in adjacent chains, resulting in a planar species in which the mean molecular planes are close to parallel and separated by a distance of ~3.5 Å, close to that of the planes in graphite.

**Keywords:** Zn(II), Cd(II) and Hg(II) Complexes; Crystal structure; 2,2'-Biquinoline (bq) ligand

### INTRODUCTION

The ability of zinc(II), cadmium(II) and mercury(II) salts to form a wide variety of 1 : 1 and 1 : 2 complexes with neutral ligands is well documented [1–5]. The most common neutral donors are phosphine and amine derivatives. Most of these complexes contain halide ions, but in contrast the thiocyanate ion has rarely been reported [6–8]. This ion is an ambidentate ligand and the coordination mode depends on the nature of the metal center. Hence N-donor atoms are found in Zn complexes, while in mercury(II) complexes, the S atom is the expected ligating site [9]. In part one of our current study, we reported the preparation and characterization of a series of 1 : 1 and 1 : 2 Zn(II), Cd(II) and Hg(II) complexes [10,11]. Here, we want to show the nature of adducts formed between Zn(II), Cd(II) and Hg(II) ions and the 2,2'-biquinoline (bq) ligand.

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## EXPERIMENTAL

### Physical Measurements

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

### Preparation of [Hg(bq)(SCN)<sub>2</sub>]

The compound [Hg(bq)(SCN)<sub>2</sub>] was obtained by reacting 2,2'-biquinoline (0.512 g, 2 mmol) with mercury(II) thiocyanate (0.316 g, 1 mmol) in methanol (5 mL) at room temperature with stirring for 48 h. The white solid formed was filtered off and dried under vacuum. Yield: 0.343 g, 60%. M.p.: 210°C. Anal. Calc. for C<sub>20</sub>H<sub>12</sub>N<sub>4</sub>S<sub>2</sub>Hg: C, 41.95; H, 2.10; N, 9.80 Found: C, 42.60.99; H, 2.20; N, 9.23%. IR (KBr, cm<sup>-1</sup>);  $\nu(\text{C-H})_{\text{ar}}$  3060,  $\nu(\text{SCN})$  2070,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1610, 1530.

The crude product was dissolved in CH<sub>3</sub>CN (10 mL) benzene (4 mL) and Et<sub>2</sub>O was diffused into the solution, forming a mixture of white precipitate and light yellow crystals.

### Preparation of [Zn(bq)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

The complex [Zn(bq)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared by dissolving 0.263 g (1 mmol) zinc(II) nitrate and excess sodium perchlorate in distilled water and then adding an alcoholic solution of 2,2'-biquinoline ligand (0.512 g, 2 mmol). The resulting solution was stirred for 7 h at room temperature, and then allowed to stand for 3–4 d in a refrigerator. A white powder of the desired product precipitated, was filtered off, washed with acetone and ether, and air dried (0.426 g, yield 55%), m.p. 226°C. Anal. Found: C, 55.42; H, 3.50; N, 7.83. Calc. for C<sub>36</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>8</sub>Zn: C, 55.67; H, 3.10; N, 7.21%. IR (KBr, cm<sup>-1</sup>);  $\nu(\text{C-H})_{\text{ar}}$  3060,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1605, 1516,  $\nu(\text{ClO}_4)$  1090.

### Preparation of [Cd(bq)<sub>2</sub>Cl<sub>2</sub>]

This complex was prepared by dissolving CdCl<sub>2</sub> (0.274 g, 1.5 mmol) in distilled water (15 mL) and adding an alcoholic solution of 2,2'-biquinoline (0.768 g, 3 mmol). The resulting solution was stirred for 3 h at room temperature, and then allowed to stand for 2–3 d in a refrigerator (*ca.* 6°C). A white powder of the desired product precipitated, was filtered off, washed with acetone and ether and air dried (0.728 g, yield 70%), m.p. 260°C. Anal. Found: C, 61.88; H, 3.25; N, 7.89. Calc. for C<sub>36</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Cd: C, 62.15; H, 3.45; N, 8.05%. IR (KBr, cm<sup>-1</sup>);  $\nu(\text{C-H})_{\text{ar}}$  3065,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1615, 1519.

### Determination of the Structure

Crystallographic measurements were made at 110(2) K for [Hg(bq)(SCN)<sub>2</sub>] using a Siemens R3m/V diffractometer. The intensity data were collected within the range  $2.26 \leq \theta \leq 30.03^\circ$  using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Accurate unit cell parameters and orientation matrix for data collection were obtained

from least-squares refinement. Intensities of 34 176 unique reflections were measured, from which 5428 with  $I > 2\sigma(I)$  were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ .

Hydrogen atom positions were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter. The values of  $R$ ,  $R_w$ , with a goodness-of-fit on  $F^2$  0.966 are 0.03016, 0.0741, respectively. The final difference density map showed a maximum peak and hole of 2.895,  $-3.066 \text{ e } \text{\AA}^{-3}$ . Corrections for the Lorentz and polarization effects, as well as the empirical correction for absorption using the semi-empirical from equivalent programs, were applied. All structural calculations were carried out with a PDP-11/23 + computer using the SDP-PLUS program package [12,13].

Crystal data and structure refinement and selected bond lengths and angles are given in Tables I and II. Anisotropic thermal parameters, observed and calculated structure

TABLE I Crystal data and structure refinement for  $[\text{Hg}(\text{bq})(\text{SCN})_2]$ 

Empirical formula	$\text{C}_{23}\text{H}_{15}\text{HgN}_4\text{S}_2$
Formula weight	612.10
Temperature (K)	110(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
$a$ ( $\text{\AA}$ )	11.186(5)
$b$ ( $\text{\AA}$ )	15.137(7)
$c$ ( $\text{\AA}$ )	12.3556(6)
$\beta$ ( $^\circ$ )	100.284(10)
Volume ( $\text{\AA}^3$ )	2058.3(6)
$Z$	4
Density (calculated) ( $\text{Mg m}^{-3}$ )	1.975
Absorption coefficient ( $\text{mm}^{-1}$ )	7.699
$F(000)$	1172
Crystal size ( $\text{mm}^3$ )	$0.2 \times 0.2 \times 0.2$
Theta range for data collection	2.26 to 30.03
Index ranges	$-15 \leq h \leq 15$ , $-21 \leq k \leq 21$ , $-17 \leq l \leq 17$
Reflections collected	12 056
Independent reflections [ $R(\text{int}) = 0.0574$ ]	34 176
Completeness to theta = 30.060	99.0%
Absorption correction	Semi-empirical from equivalents
Max., min. transmission	0.07, 0.02
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5966/0/256
Goodness-of-fit on $F^2$	0.966
Final $R1$ , $wR2$ for 5428 refl. [ $I > 2\sigma(I)$ ]	0.0301, 0.0741
$R1$ , $wR2$ (all data)	0.0330, 0.0759
Largest diff. peak, hole ( $\text{e } \text{\AA}^{-3}$ )	2.895, $-3.066$

TABLE II Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{Hg}(\text{bq})(\text{SCN})_2]$ 

Hg(1)–N(1)	2.35(3)
Hg(1)–N(2)	2.37(3)
Hg(1)–S(2L)	2.44(11)
Hg(1)–S(1L)	2.47(12)
N(1)–Hg(1)–N(2)	70.31(10)
N(1)–Hg(1)–S(2L)	119.65(7)
N(2)–Hg(1)–S(2L)	112.42(7)
N(1)–Hg(1)–S(1L)	103.68(7)
S(2L)–Hg(1)–S(1L)	134.63(4)

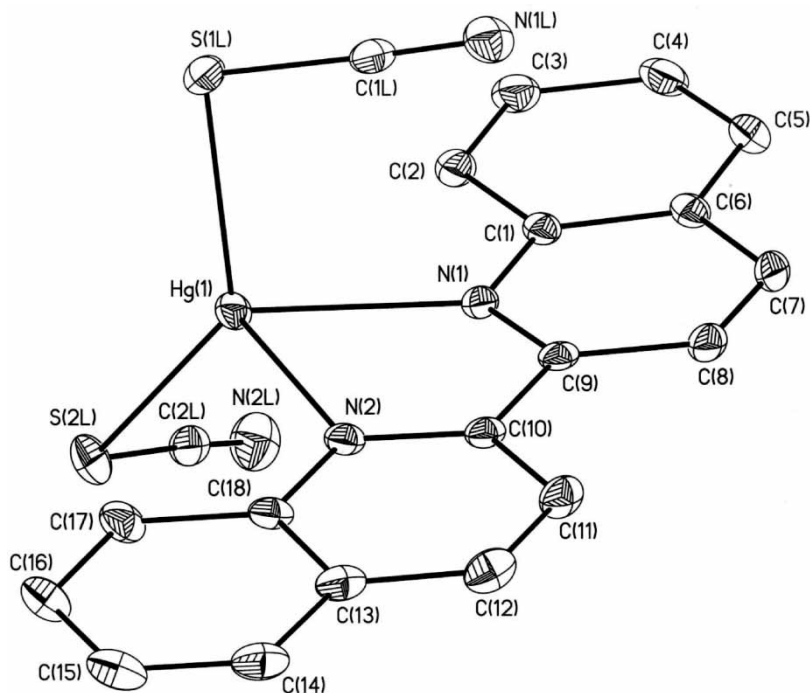


FIGURE 1 ORTEP diagram of  $[\text{Hg}(\text{bq})(\text{SCN})_2]$ .

factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. An ORTEP diagram and a perspective view of the packing in the unit cell are shown in Figs. 1 and 2.

## RESULTS AND DISCUSSION

### Synthesis and Spectroscopic Properties of the Complexes

Reaction of  $\text{Hg}(\text{SCN})_2$ ,  $\text{Zn}(\text{ClO}_4)_2$  and  $\text{CdCl}_2$  with 2,2'-biquinoline provided powder materials analyzing as  $[\text{Hg}(\text{bq})(\text{SCN})_2]$ ,  $[\text{Zn}(\text{bq})_2](\text{ClO}_4)_2$  and  $[\text{Cd}(\text{bq})_2\text{Cl}_2]$ , respectively. The IR spectrum of the  $[\text{Hg}(\text{bq})(\text{SCN})_2]$  complex shows  $\nu(\text{SCN})$  at  $2070\text{ cm}^{-1}$  and the  $[\text{Zn}(\text{bq})_2](\text{ClO}_4)_2$  complex shows  $\nu(\text{ClO}_4)$  at  $1090\text{ cm}^{-1}$ . Isolation of  $[\text{Hg}(\text{bq})_2(\text{SCN})_2]$  was not successful and each time a 1:1 adduct was isolated. All three complexes have  $d^{10}$  electronic configuration and there are no d-d electronic transitions in these complexes.

### Crystal Structure of $[\text{Hg}(\text{bq})(\text{SCN})_2]$

A view of the ORTEP diagram is shown in Fig. 1 and selected bond lengths and angles are given in Table II. The complex is built up of a monomeric  $\text{Hg}(\text{SCN})_2$  unit [ $\text{Hg}(1)\text{--S}(1\text{L})$  2.47 and  $\text{Hg}(1)\text{--S}(2\text{L})$  2.43 Å], with one 2,2'-biquinoline ligand coordinated to the Hg atom via the two N atoms giving rise to a five-membered chelate ring [ $\text{Hg}(1)\text{--N}(1)$  2.35 Å and  $\text{Hg}(1)\text{--N}(2)$  2.37 Å], in a distorted tetrahedral environment. The smallest

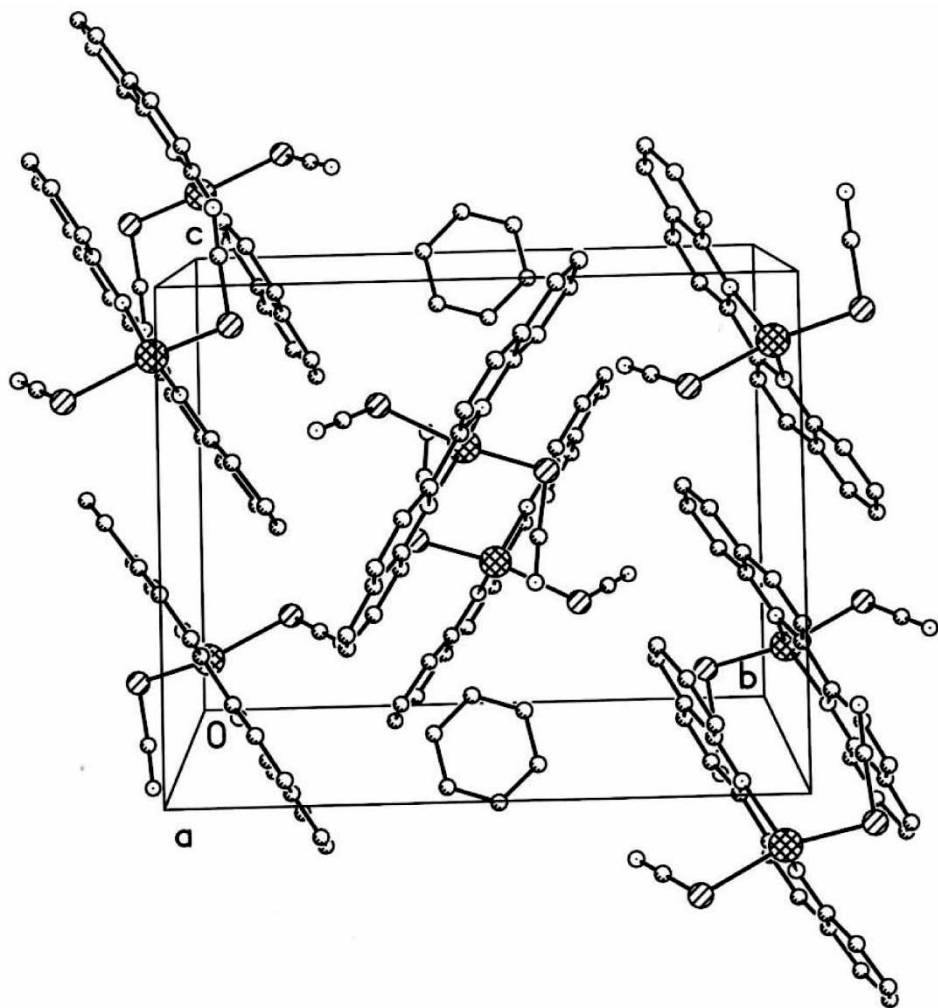


FIGURE 2 The unit cell diagram showing  $\pi$ - $\pi$  stacking interaction in  $[\text{Hg}(\text{bq})(\text{SCN})_2]$ .

and largest bond angles around the Hg atoms are  $\text{S}(2\text{L})\text{-Hg}(1)\text{-S}(1\text{L})$   $134.63^\circ$  and  $\text{N}(1)\text{-Hg}(1)\text{-N}(2)$   $70.31^\circ$ . In contrast, in the lead(II) complexes, the thiocyanate ions are coordinated via the N atom [10]. In mercury complexes such as  $[\text{Hg}(\text{DPBTZ})(\text{SCN})_2]$  (DPBTZ = 2,2'-diphenyl-4,4'-bithiazole) [12] and  $[\text{Hg}(\text{DABTZ})(\text{SCN})_2]$  (DABTZ = 2,2'-diamino-4,4'-bithiazole) [11], the thiocyanate ions are coordinated via S atoms. This shows that  $\text{Hg}^{2+}$  ion is softer than  $\text{Pb}^{2+}$  ion. There are two benzene molecules in the unit cell of this complex. The benzene solvent was used for isolating single crystals suitable for X-ray crystallography.

There are differences between the Hg-N distances in  $[\text{Hg}(\text{DPBTZ})(\text{SCN})_2]$  and  $[\text{Hg}(\text{bq})(\text{SCN})_2]$  or  $[\text{Hg}(\text{DABTZ})(\text{SCN})_2]$  {2.30 Å for  $[\text{Hg}(\text{DABTZ})(\text{SCN})_2]$  and 2.35 Å for  $[\text{Hg}(\text{bq})(\text{SCN})_2]$  compared with 2.50 Å for  $[\text{Hg}(\text{DPBTZ})(\text{SCN})_2]$ . These variations may be a consequence of the initial electron withdrawing effect of the phenyl rings and also their spatial effects.

The striking similarity of [Hg(DPBTZ)(SCN)<sub>2</sub>] and [Hg(DABTZ)(SCN)<sub>2</sub>] with the [Hg(bq)(SCN)<sub>2</sub>] complex is in the  $\pi$ - $\pi$  stacking [14,15] interaction between the parallel aromatic rings of adjacent chains as shown in Fig. 2. These planar species have mean molecular planes almost parallel and separated by a distance of  $\sim 3.5$  Å, close to that of the planes in graphite.

### Acknowledgments

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### Supplementary Material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallographic Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 208607.

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