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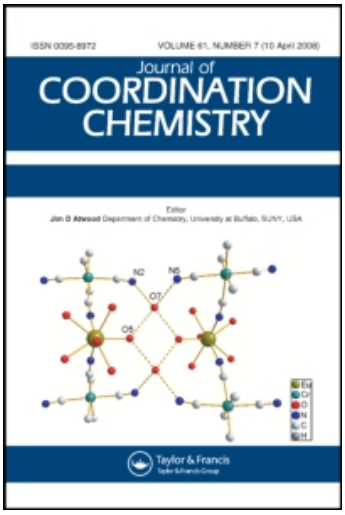

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Synthesis, crystal structure and magnetic properties of a novel complex containing a diamagnetic metal ion and thiazole-substituted nitronyl nitroxide radicals

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The synthesis, crystal structure and magnetic properties of a novel diamagnetic metal complex containing thiazole-substituted nitronyl nitroxide radicals, $[HgCl_2(NIT2\text{-}thz)_2]$ (NIT2-thz = 2-(2′-thiazole)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), is reported. The mercury(II) ion has distorted tetrahedral coordination involving two chloride atoms and two thiazole nitrogen atoms. Magnetic susceptibility data show that there are intramolecular antiferromagnetic interactions between the radicals in the complex.

Keywords: Crystal structure; Nitronyl nitroxide radical; Mercury(II) complex; Magnetism

1. Introduction

There has been increasing interest in the study of molecule-based magnetism in recent years [1, 2], and nitronyl nitroxide radicals have been widely used as molecular units in the design and synthesis of molecular magnetic materials [3, 4]. The magnetic properties of complexes of nitronyl nitroxide radicals with paramagnetic metal ions have been studied extensively [5–7]. Meanwhile, investigations on diamagnetic metal complexes with radicals have also attracted attention because of antiferro- or ferromagnetic interactions of radicals through the diamagnetic metal ions in the complexes [8, 9].

To investigate the magnetic exchange interactions between radicals through the diamagnetic metal ion, we have used a diamagnetic metal ion as a linking agent between radicals in systems where the electronic structure of the metal ion bridge provides an orbital pathway for interradical exchange. We report here the synthesis, X-ray structure

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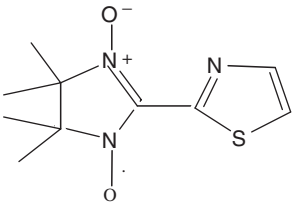

NIT2-thz

Scheme 1. Diagram of NIT2-thz.

and magnetic properties of a novel mercury(II) complex with thiazole-substituted nitronyl nitroxide radicals, $[HgCl_2(NIT2\text{-}thz)_2]$ (NIT2-thz = 2-(2′-thiazole)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, scheme 1).

2. Experimental

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All starting materials were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer instrument. IR spectra were measured using a Shimadzu IR 408 spectrophotometer in the 4000–600 cm^{-1} region, using KBr pellets. Variable-temperature magnetic susceptibilities were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants for all constituent atoms.

2.1. *Synthesis*

2,3-Dimethyl-2,3-bis(hydroxylamino)butane was prepared by a published method [10]. 2-(2′-Thiazole)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared using 2,3-dimethyl-2,3-bis(hydroxylamino)butane and 2-thiazolecarboxaldehyde as starting materials, following the method of Ullman *et al.* [11]. The complex $[HgCl_2(NIT2\text{-}thz)_2]$ was synthesized by dissolving $HgCl_2$ (0.034 g, 0.125 mmol) and NIT2-thz (0.062 g, 0.25 mmol) in 40 cm^3 of dry EtOH solvent at room temperature. The mixture was stirred for a few hours and then filtered. The dark brown filtrate was allowed to stand in the dark for 1 week, when dark brown crystals suitable for X-ray analysis were obtained. Anal. Calcd for $C_{20}H_{28}Cl_2N_6O_4S_2Hg$(%): C, 31.94; H, 3.76; N, 11.22. Found: C, 31.80; H, 3.89; N, 11.07. IR: $\nu_{thz} = 1413$, 1185 and 1136 cm^{-1}; $\nu_{N-O} = 1375\ cm^{-1}$.

2.2. *Structure determination*

A single crystal was mounted on a RAXIS-IV area detector equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the ϕ–ω scan mode. Unit cell parameters were determined from reflections in the range $2.23^\circ \leq \theta \leq 27.52^\circ$. Details concerning data collection, crystallographic data and reduction are summarized in table 1. The structure was solved by direct methods using SHELXS-97 [12]. H-atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints.

Table 1. Crystallographic data and structure refinement parameters for $[HgCl_2(NIT2\text{-}thz)_2]$.

Empirical formula	$C_{20}H_{28}Cl_{12}N_6O_4S_2Hg$
Formula weight	752.09
Crystal system	Orthorhombic
Space group	*Pccn*
a (Å)	18.289(4)
b (Å)	9.7236(19)
c (Å)	15.369(3)
β (°)	90
Volume (Å^3), *Z*	2733.2(9), 4
F(000)	1472
Crystal size (mm)	$0.28 \times 0.20 \times 0.20$
Reflections collected	7791
Independent reflections	2706
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0510$, $wR2 = 0.0921$
R indices (all data)	$R1 = 0.1204$, $wR2 = 0.1080$
Goodness-of-fit on F^2	1.115
Largest diff. peak and hole (e Å^{-3})	0.819 and −0.848

Table 2. Selected bond lengths (Å) and angles (°) for $[HgCl_2(NIT2\text{-}thz)_2]$.

Hg(1)–Cl(1)	2.318(2)	N(3)–O(2)	1.267(7)
Hg(1)–N(1)	2.635(6)	S(1)–C(3)	1.731(7)
N(2)–O(1)	1.282(8)	N(1)–C(1)	1.363(9)
S(1)–C(2)	1.681(9)	N(1)–C(3)	1.324(9)
Cl(1)–Hg(1)–Cl(1)#1	162.11(16)	Cl(1)–Hg(1)–N(1)	87.69(14)
Cl(1)#1–Hg(1)–N(1)	106.50(15)	N(1)–Hg(1)–N(1)#1	76.8(3)
C(3)–N(1)–Hg(1)	129.5(5)	C(1)–N(1)–Hg(1)	114.9(5)

#1: $-x+1/2$, $-y+1/2$, z.

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A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [12]. Reliability factors were defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and the function minimized was $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^2$, where in the least-squares calculation unit weights were used. All nonhydrogen atoms were refined anisotropically. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

The crystal structure of $[HgCl_2(NIT2\text{-}thz)_2]$ is illustrated in figure 1. The distorted tetrahedral coordination of Hg(II) is formed by two terminal chloride atoms and two nitrogen atoms of two NIT2-thz ligands. Hg–Cl and Hg–N bond lengths are 2.318(2) and 2.635(6) Å, respectively. Sulfur remains uncoordinated. The fragment O(2)–N(3)–C(4)–N(2)–O(1) is nearly planar, forming a dihedral angle of 14.5(2)° with the plane of the thiazole ring.

3.2. *Magnetic properties*

Magnetic susceptibilities, χ_M, were measured from 5 to 300 K at 10 000 G. Plots of $\chi_M T$ and χ_M versus T are shown in figure 2. The $\chi_M T$ value at room temperature

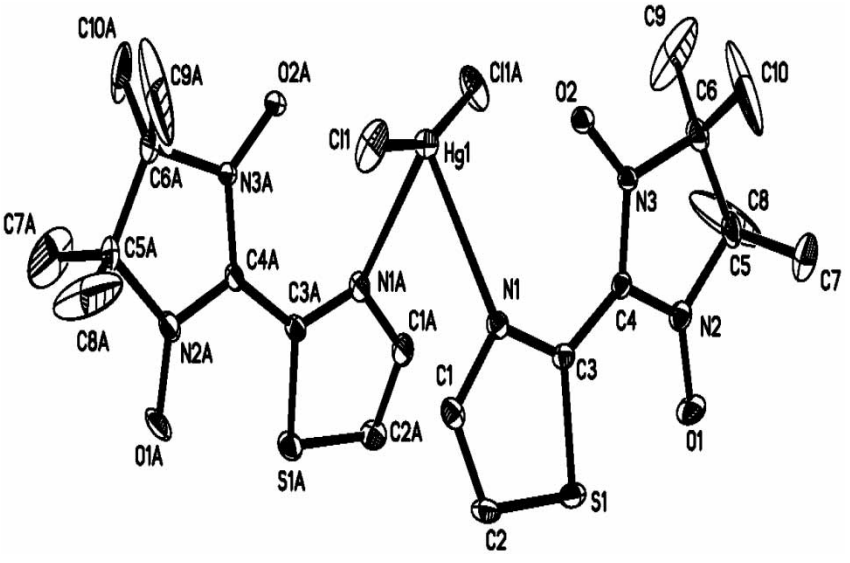

Figure 1. ORTEP drawing of $[HgCl_2(NIT2\text{-}thz)_2]$ showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

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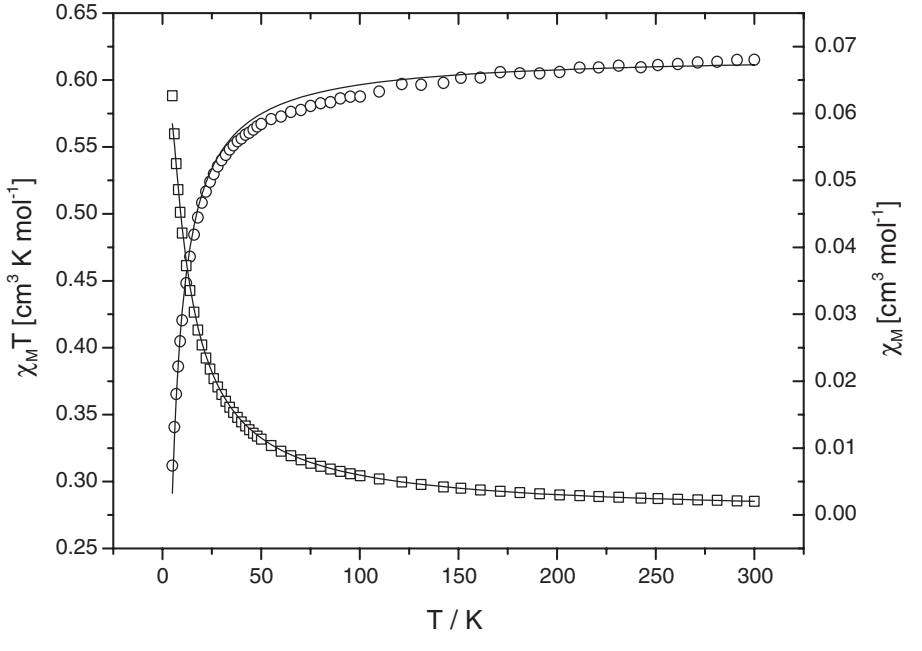

Figure 2. Temperature dependence of χ_M (□) and $\chi_M T$ (○) for $[HgCl_2(NIT2\text{-}thz)_2]$.

is 0.63 $cm^3\,mol^{-1}\,K$, lower than the spin-only value expected for two $S = 1/2$ uncoupled spin systems (0.75 $cm^3\,mol^{-1}\,K$). With cooling from 300 to approximately 100 K, the $\chi_M T$ value decreases slowly, and below approximately 100 K decreases rapidly to 0.31 $cm^3\,mol^{-1}\,K$, implying the existence of a weak antiferromagnetic spin-exchange

interaction between the NIT2-thz radicals. In the complex, two paramagnetic centers are linked by a diamagnetic metal ion and analysis of magnetic properties was performed using the Bleany–Bowers (dimer) model [13]. Magnetic data were fitted to the theoretical expression for the magnetic susceptibility expressed by the Heisenberg Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$, where J is the interaction parameter between the radicals.

$$\chi_M = \frac{2Ng^2\beta^2}{KT}[3 + \exp(-2J/KT)]^{-1}$$

The best-fitted parameters were $J = -1.69\,\mathrm{cm}^{-1}$, $g = 1.95$, $R = 8.68 \times 10^{-4}$, where R is defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum(\chi_M)^2_{obs}$. The results indicate that the diamagnetic metal ion provides an orbital pathway for interradical exchange, but exchange is weak. This is in agreement with complexes reported previously with similar structures [8].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204118. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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