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Solution behavior of Hg(II)-cystamine by Uv-Vis and ^{199}Hg NMR

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The combination of $HgCl_2$ with the disulfide salt of 2-aminoethanethiol (cystamine dihydrogen dichloride) in water yields a two-dimensional chain $\{[HgCl_4][(NH_3CH_2CH_2S-)_2]\}_n$ **(1)**. It consists of six-coordinate Hg in $[HgCl_4]_n$ units with bridging and termainal Cl atoms. The disulfide groups, $(NH_3CH_2CH_2S-)_2$ are held between the $[HgCl_4]_n$ chain with weak S–S interactions. The chlorides in the $[HgCl_4]_n$ units are involved in intermolecular hydrogen bonding to yield a three-dimensional network. A similar reaction with the reduced form of cystamine (2-amino ethanethiol) yields a linear Hg(II)-bis-thiolate, $[Hg(SCH_2CH_2NH_3]^{2+}$ (**2**). When compound **1** is combined with two equivalents of NaOH it rearranges to **2** as indicated by ^{199}Hg NMR and Uv-Vis.

Keywords: $HgCl_2$; Cystamine; Disulfide; ^{199}Hg NMR; Uv-Vis

1. Introduction

All forms of mercury are toxic to various tissues and organs [1]. The inorganic form, Hg^{2+} is the most common one in occupational and environmental settings. Inorganic mercury alters proteins by interacting with the thiol and disulfide groups. This induces oxidative stress, lipid peroxidation, mitochondrial dysfunction and a change in heme metabolism [1]. Disulfide bonds (–SS–) are involved in the stabilization of protein structure. Thus, it is important to understand how disulfides interact with metal ions, and especially mercury [2]. The organomercury ion promoted cleavage of the disulfide bond is well clarified [3,4] but the coordination chemistry of Hg^{2+} with disulfide is limited compared to free thiols [5,6]. Since the disulfide linkage of cysteine (as cystine) is probably the only covalent cross-linkage in most of the proteins, the interaction of mercury with the –SS– moiety could a have profound effect on the tertiary structure. The Hg^{2+} ion is one of the common electrophiles in –SS– bond cleavage beside H^+ and Ag^+ [7]. The two fundamental mechanistic pathways for the heterolytic cleavage of the disulfide bond are a) attack at S by the nucleophile with displacement of RS^-

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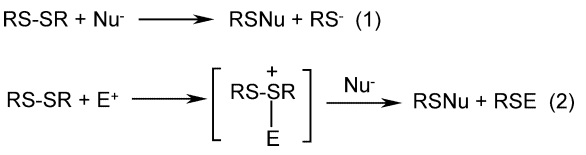


Scheme 1. Mechanistic pathways for disulfide cleavage.

(equation (1)) and b) the combined action of both an electrophile and a nucleophile (equation (2)), as shown in scheme 1.

There are a limited number of documented metal-organic disulfide salts. For example, $[HgI_4](C_{18}H_{26}N_2S_2)$, $[\{(CH_3)_2HN(CH_2)_3S\}_2][MX_4]$ (M = Zn(II), Cd(II), Hg(II) and X = Cl or Br) and $[(C_5H_9NH(CH_3)S)_2CuCl_4]$ [8–10]. Also, the combination of various Hg^{2+} salts with cyclic and linear disulfides including α-lipoic acid and di-*n*-butyl disulfide have been reported but not studied in detail [11].

Here we report the results from the combination of $HgCl_2$ with cystamine dihydrogen dichloride (cysta), which is very similar to the biologically important moiety, cystine (decarboxylated). Addition of $HgCl_2$ with cysta in a 1:2 ratio in DI water yields a polymeric structure with the repeating unit, $[HgCl_4][(NH_3CH_2CH_2S-)_2]$ (**1**). A similar reaction with the reduced from of cysta yields a linear bis-thiolate compound, $[Hg(SCH_2CH_2NH_3)]^{2+}$ (**2**) [12]. It was quite interesting to observe that in the presence of NaOH, compound **1** rearranges to **2**. This observation can be related to the mechanism proposed in equation (2), where the intermediate, in the presence of a nucleophile, yields a metal-thiolate compound.

2. Experimental section

The reactions were carried out at room temperature in deaerated DI water under a flow of nitrogen. The ligand, cystamine dihydrogen dichloride (TCI America) was dried under vacuum prior to use. The reagent $HgCl_2$ (Fischer Scientific) was used as received. ^1H and ^{13}C NMR data was obtained with JEOL-GSX-400 and 270 instruments operating at 200 and 400 MHz using d_6-DMSO as a solvent and tetramethylsilane as reference. The IR data was recorded as KBr pellets on a Mattson Galaxy 5200 FT-IR instrument between 400–4000 cm^{-1}. Mass Spectral (EI-MS) data were obtained at the University of Kentucky Mass Spectrometry Facility. The UV-Vis studies were performed on an Agilent HP 8453 instrument by using 5 mM solution in DI water. The $^{199}Hg\{^1H\}$ NMR spectrum of 0.5 M of **1** and **2** in d_6-DMSO was collected at 25°C on a Varian INOV 400 MHz instrument with 4-Nucleus Autoswitchable 5 mm Probe and referenced to 1 M $HgCl_2$ in DMSO at −1500 ppm [13,14] and checked against external 0.1 M $Hg(ClO_4)_2$ in D_2O (−2250 ppm) [15]. Colorless crystals of **1** were obtained in quantitative yield from the filtrate by slow evaporation at room temperature. X-ray diffraction data were collected at 90 K on the Nonius Kappa CCD diffractometer unit using Mo-Kα radiation from regular shaped crystals mounted in Paratone-N oil on glass fibers.

2.1 *$[HgCl_4][(NH_3CH_2CH_2S-)_2]$ (1)*

To a stirring solution of cystamine dihydrogen dichloride (10 mmol, 2.25 g) in DI water (20 ml) was added $HgCl_2$ (5 mmol, 1.35 g) to obtain a white precipitate.

The resulting solution was stirred overnight. The white precipitate was removed and dried well. Slow evaporation of the filtrate yielded colorless crystals (table 1). Crystalline Yield: 2.7 g (58%). mp 190°C (dec without melting). ^{1}H NMR (DMSO, 200 MHz, ppm): δ 2.93 (t, 2H, CH_2N), δ 3.12 (t, 2H, CH_2S), δ 7.85 (s, 3H, NH_3). ^{13}C NMR (DMSO, 200 MHz, ppm): δ 33.7 (CH_2S), δ 37.8 (CH_2N). IR (KBr, ν/cm^{-1}): 3448, 3126, 1631, 1580, 1479, 1324, 1262, 1091, 935, 807, 667. EIMS (m/z (%)): 92, ($[SSCH_2CH_2]^+$, 86); 109, ($[SSCH_2CH_2NH_3]^+$, 75); 154, ($[(NH_3CH_2CH_2S-)_2]^+$, 95); 270, ($[HgCl_2]^+$, 15); 351, ($[\{Hg\}\{(NH_3CH_2CH_2S-)_2\}]^+$, 5). Anal. calcd for $[HgCl_4][(NH_3CH_2CH_2S-)_2]$: C, 9.672; H, 2.841; N, 5.640. Found: C, 9.594; H, 2.821; N, 5.552.

3. Result and discussion

In the ^{1}H NMR spectrum, no significant changes in the ppm values are observed for either CH_2S (3.12 ppm) or CH_2N (2.93 ppm) protons when compared to the free ligand. The integration for amine protons at 7.85 ppm indicates the presence of the protonated group (NH_3^+). Similar observations are also made in ^{13}C NMR spectrum (CN, 33.7 and CS, 37.8 ppm). In the IR spectrum, no significant changes in the C–S and S–CH_2 stretches are observed compared to free ligand. This indicates that the chemical environments of the disulfide group in the compound and in the free ligand are similar. The ammonium bands at 2938 – 3130, 1561 – 1583 cm^{-1} and no change in the C–N stretching indicated the presence of an uncoordinated ammonium group. Also, peaks at 1468 and 1594 cm^{-1} could be assigned to the symmetric deformation and the degenerate deformation modes, respectively, for the $-NH_3^+$ group. Similar peaks have been observed for mercury compounds with L-cysteine (1487 and 1606 cm^{-1}) and L-cysteine methyl ester (1495 and 1582 cm^{-1}) [16].

Table 1. Crystal data for **1**.

Data	**1**
Empirical Formula	$C_4H_{14}Cl_4HgN_2S_2$
Formula Weight	496.68
Temperature (K)	90.0
Wavelength Å	0.71073
Crystal System	Orthorhombic
Space Group	c m c a
a (Å)	11.2088(3)
b (Å)	10.8632(4)
c (Å)	22.3867(6)
$\alpha = \beta = \gamma$ (°)	90.0
Volume (Å^3)	2725.88(14)
Z	8
Density Calculated (mg/m^3)	2.421
Absorption Coefficient (mm^{-1})	12.347
F(000)	1856
Crystal Size	0.10 × 0.05 × 0.03
Reflection Collected	11487
Independent Reflections	1629(R(int) = 0.0436)
Refinement Method	Full-matrix least-square on F^2
Goodness of fit on F^2	1.089
Final R indices [I > 2sigma(I)]	$R_1 = 0.0251$, $wR_2 = 0.0535$
R indices (all data)	$R_1 = 0.0343$, $wR_2 = 0.0578$

The λ_{max} for **1** at 260 nm (figure 1) is most probably due to the disulfide moiety, as λ_{max} for $HgCl_2$ is not observed in this range ($\lambda_{max} = 200$ nm) [17]. The λ_{max} for **2** is observed around 270 nm, which is due to the S → Hg LMCT. However, low-energy charge transfer bands for two- or three-coordinate Hg(II)-thiolates and Hg(II)-thiolates with distorted tetrahedral geometry fall in the range of 230–250 nm and 280–310 nm respectively [6,18,19]. Hence, the significant shift in the λ_{max} is most probably due to the close proximity of two Cl ions in the solution, which might result in equilibrium between two- and four-coordinate compound. The addition of two equivalents of base to **1** shift the λ_{max} value to 270 nm (**1Nu**$^-$), which coincides with the λ_{max} value observed for **2**. This suggests that compound **1** in the solution rearranges to **2** according to equation (2) (scheme 2).

Due to a large chemical shift range, stronger heteronuclear coupling and faster relaxation time, there is a considerable current interest in employing the ^{199}Hg nucleus as a metalloprobe and expanding the available data [20]. The spectrum for 0.5 M of **1** and **1Nu**$^-$ were obtained in d_6-DMSO employing 1 M $HgCl_2$ in DMSO as internal reference [13,14]. The peak due to six-coordinate Hg^{2+} in **1** is observed at −1144 ppm (figure 2). Addition of base to **1** resulted in a shift to −591 ppm (**1Nu**$^-$), which is comparable to the shift observed for **2** (−659 ppm) [21]. The significant difference in

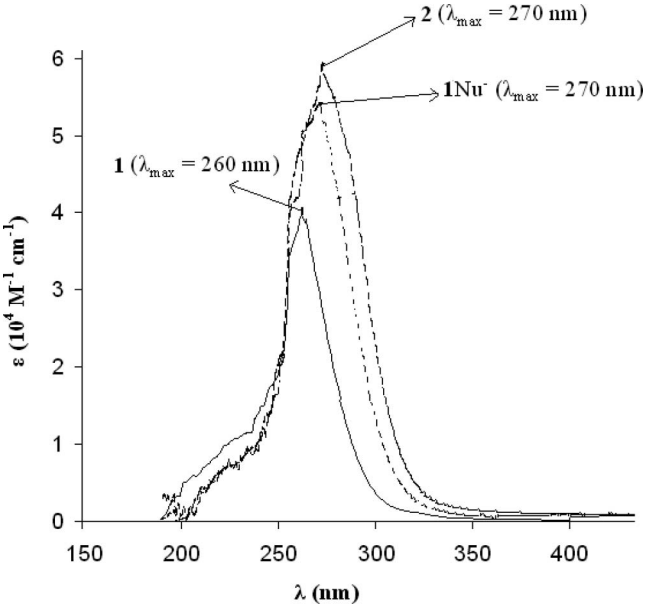
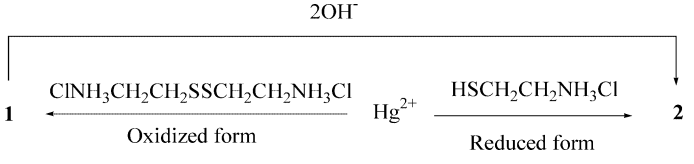


Figure 1. Electronic spectra of 5 mM solution of **1**, **2** and **1**Nu$^-$ in DI water.



Scheme 2. Scheme showing conversion of **1** to **2**.

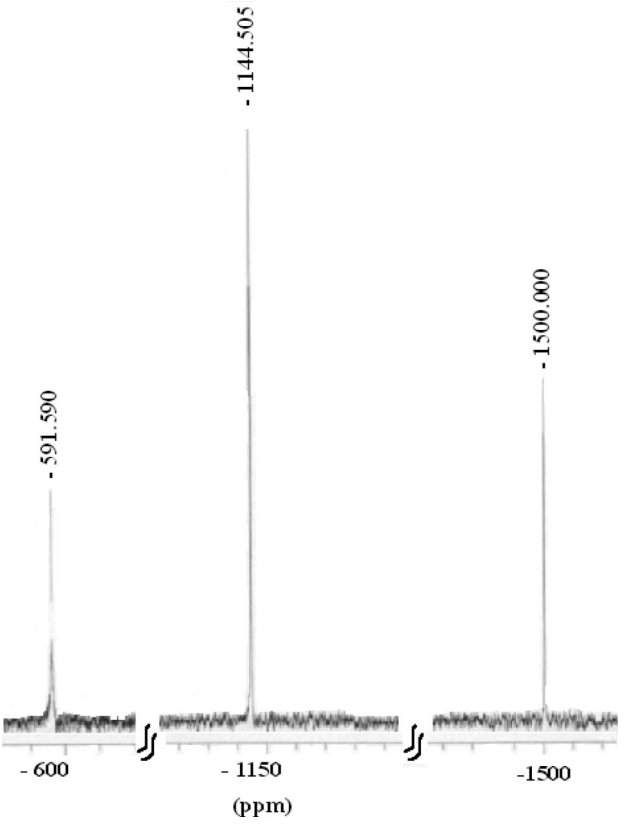


Figure 2. ^{199}Hg NMR spectra of 0.5 M **1** (−1144 ppm) and **1Nu**$^-$ (−591 ppm) in d_6-DMSO at 25°C with 1 M $HgCl_2$ (−1500 ppm) as reference.

the shift can be attributed to the fact that ^{199}Hg NMR is highly solvent- and concentration-dependent [22].

The crystal structure of **1** is quite unique since the reaction of Hg^{2+} with −SS− containing ligands usually leads to an Hg−S bonded compound. This is observed in $[HgCl_2(Me_2S_2)]$ for instance [23]. The absence of Hg−N contacts in **1** is also in contrast to that observed in polymeric [Hg(bis(2-pyridyl)disulfide)X_2] (X = Cl and Br), where the repeating units are held together with −SS− bonds with Hg^{2+} attached to the N atom [24]. A similar observation is also made in the adducts of Zn^{2+}, Cd^{2+} and Ni^{2+} with D-penicillamine disulfide, oxidized glutathione and L-cysteinylglycine disulfide, where the amino, carboxylate and amide functional groups are exclusively involved in metal binding [25,26]. The absence of Hg−N in **1** is due to the protonated amine groups. The Hg atom is attached to four bridging and two terminal Cl atoms forming a two-dimensional $[HgCl_4]^{2-}$ layer (figure 3). The $Hg-Cl_{bridging}$ distances (avg 2.803 Å) are shorter and the $Hg-Cl_{terminal}$ distance (avg 2.439 Å) are longer compared to the corresponding distances observed in $[HgCl_2(Me_2S_2)]$ (3.115 Å and 2.299 Å, respectively) [23]. A similar trend is also observed in compounds containing polymeric $[HgCl_6]$ octahedra such as $[NH_3(CH_2)_nNH_3HgCl_4]$ (n = 3, 5) (avg 2.8 Å (bridging) and 2.4 Å (terminal)) [27,28].

The geometry around Hg is octahedral with Cl—Hg—Cl angles close to 90°, as required for a perfect octahedral structure (table 2). However, the repeating $[HgCl_4]$ units are neither parallel nor perpendicular to each other with torsion angles of 13.51° and 104.9° for the Cl—Hg—Cl—Hg′ unit. This is in contrast to the geometry associated with the $[HgCl_4]$ unit in $K_{2.51}(NH_4)_{1.49}Hg_3Cl_{10}\cdot 2H_2O$[29]. The distortion can be attributed to the involvement of both terminal and bridging Cl atoms in intermolecular hydrogen bonding.

The cysta groups are present between the chains with the amine groups pointing toward the Cl atoms. The $NH_3CH_2CH_2S$- units are characterized by a static disorder with C, S and N atoms occupying two equivalent positions. All the amine hydrogens are involved in hydrogen bonding with the Cl atoms. The average NH—Cl distances in **1** (3.332 Å) are within the range (3.23 – 3.57 Å) observed for similar hydrogen-bonded

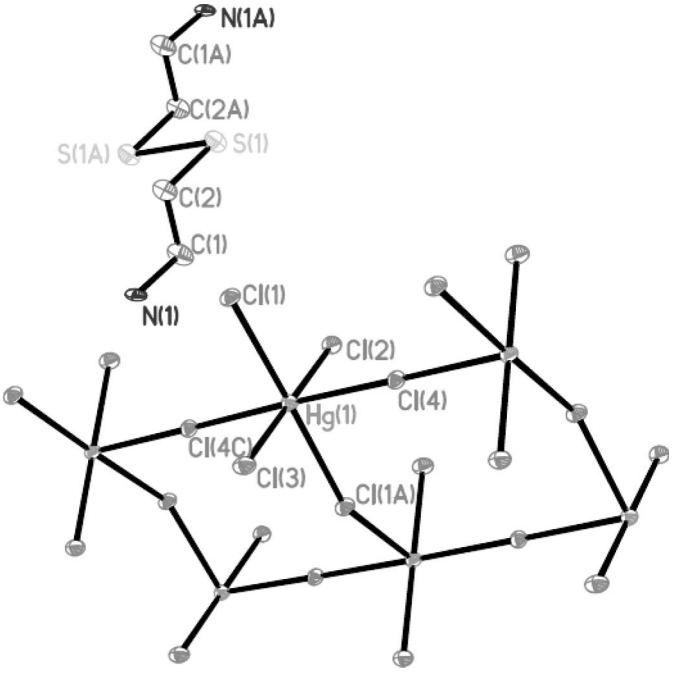


Figure 3. View of **1** with 50% thermal ellipsoid.

Table 2. Bond distances (Å) and angles (°) for **1**.

Hg(1)—Cl(3)	2.4348(14)	Hg(1)—Cl(2)	2.4449(14)
Hg(1)—Cl(4)′	2.8026(14)	Hg(1)—Cl(4)	2.8026 (14)
Hg(1)—Cl(1)′	2.8035(13)	Hg(1)—Cl(1)	2.8066(13)
Cl(1)—Hg(1)′	2.8035(13)	Cl(4)—Hg(1)′	2.8026 (14)
S(1)—S(1)′	2.409(4)		
Cl(3)—Hg(1)—Cl(2)	179.85(4)	Cl(3)—Hg(1)—Cl(4)	89.193(8)
Cl(2)—Hg(1)—Cl(4)	90.806(8)	Cl(3)—Hg—Cl(1)	88.76(4)
Cl(2)—Hg(1)—Cl(1)	91.39(4)	Cl(4)—Hg(1)—Cl(1)	90.49(2)
Cl(1)—Hg(1)—Cl(1)′	178.104(15)	Hg(1)—Cl(1)—Hg(1)′	151.08(6)
Hg(1)—Cl(4)—Hg(1)′	179.42(5)		

compounds (table 3) [27–29]. The intermolecular hydrogen bonding create a three-dimensional extended network (figure 4). The presence of weak S—S interactions (3.217 Å) among the cysta groups is quite interesting as similar interactions have not been observed in $[HgCl_2(Me_2S_2)]$ and [Hg(bis(2-pyridyl)disulfide)X_2] (X = Cl and Br) [23,24]. This can be attributed to the presence of an Hg—S covalent bond in the latter compounds. These distances are slightly larger than those observed in Naptho[1,8–b,c]–1,5dithiocin (avg 2.926 Å) [30] but smaller than twice the van der Waals radius of S (3.70 Å) [31].

Table 3. Hydrogen bonding geometry associated with **1**.

D—H—A	D—H (Å)	H—A (Å)	D—A (Å)	DHA (°)
N1—H1A—Cl4	0.91	2.66	3.39(4)	138.5
N1—H1A—Cl1	0.91	2.74	3.37(4)	127.5
N1—H1B—Cl4	0.91	2.37	3.24(3)	159.8
N1—H1C—Cl2	0.91	2.47	3.33(4)	157.6
N1′—H12′—Cl3	0.91	2.72	3.41(4)	134.1
N1′—H13′—Cl2	0.91	2.57	3.34(4)	142.3
N1—H13′—S1′	0.91	2.72	3.16	111.4

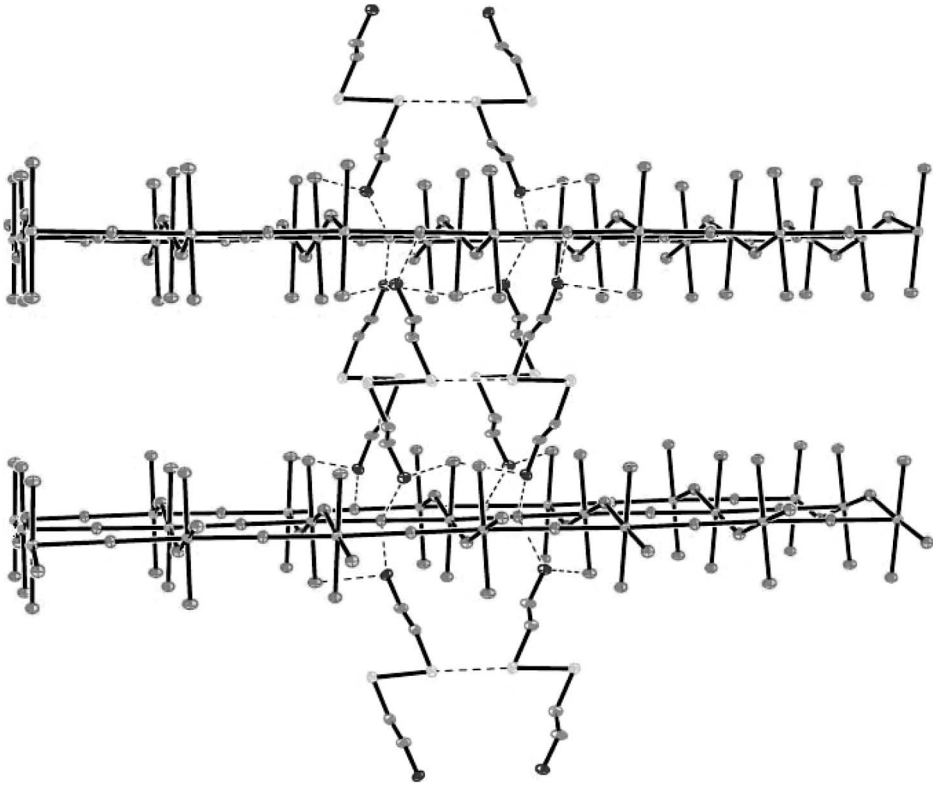


Figure 4. Polymeric chain of **1** with weak interactions shown with dotted lines.

4. Conclusion

The absence of a sulfur interaction with Hg^{2+} in **1** is somewhat surprising in light of the structural data availabe for disulfide metal adducts with mercury. In all the previous cases the sulfur atoms are involved in metal coordination in bidentate, tridentate or tetradentate fashion along with halides. The conversion of **1** to **2** in the presence of a base raises the question regarding the structure of the intermediate. If Hg^{2+} is involved with the disulfide with an active Hg—S covalent bond in the intermediate, then the addition of a nucleophile might not form the Hg(II)-bis-thiolate compound. It is possible that Hg^{2+} exists as an inorganic salt along with the disulfide in the intermediate. Such studies with the reported Hg^{2+}-disulfide compounds require further attention.

5. Supporting information available

Syntheses, characterization information, additional figures, tables, ^{199}Hg NMR of **1** and **2** and crystals data. Crystallographic data for the structures analysis for compounds **1** has been deposited with the Cambridge Crystallographic Data Center, CCDC No, 280072.

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