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Effect of functionlization of N,Ndibenzyldithiocarbamate: synthesis, spectral and structural studies on bis(N-benzyl-N-(4methoxybenzyl)dithiocarbamato-S,S')zinc(II) and bis(N-benzyl-N-(4-cholrobenzyl)dithiocarbamato-S,S')cadmium(II) and their use for the preparation of MS (M = Zn, Cd)

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Effect of functionlization of *N*,*N*-dibenzyldithiocarbamate: synthesis, spectral and structural studies on bis(*N*-benzyl-*N*-(4-methoxybenzyl)dithiocarbamato-S,S')zinc(II) and bis(*N*-benzyl-*N*-(4-cholrobenzyl)dithiocarbamato-S,S')cadmium(II) and their use for the preparation of MS (M = Zn, Cd)

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ABSTRACT

Bis(N-benzyl-N-(4-methoxybenzyl)dithiocarbamato-S,S')zinc(II) (1) and bis(N-benzyl-N-(4-chlorobenzyl)dithiocarbamato-S,S')cadmium(II) (2) have been prepared and characterized by elemental analysis, IR and NMR (¹H and ¹³C) spectroscopy and single-crystal X-ray analysis. Complexes 1 and 2 exist as monomer and dimer, respectively. Crystal structures of 1 and 2 confirm the presence of four coordinated zinc in a distorted tetrahedral arrangement and five coordinated cadmium in a distorted square pyramid arrangement, respectively. Both the complexes are further stabilized by various interactions such as C–H···S, C–H···N, C–H···O and C–H··· π (chelate). C–H···O interaction leads to the formation of dimer in complex 1. In complex 2, C–H $\cdots\pi$ (chelate) interaction runs in opposite directions which results in the polymeric chain. ZnS and CdS have been prepared from 1 and 2, respectively, and characterized by powder X-ray diffraction, SEM, UV–Vis and fluorescence spectroscopy. The X-ray diffraction pattern confirms the wurtzite phase of as-prepared ZnS and CdS.



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1. Introduction

Studies on metal dithiocarbamate complexes continue to attract the attention of inorganic chemists due to their wide applications such as in analytical chemistry, [1,2,3] catalysis, [4,5]

organic synthesis, [6] accelerator for vulcanization of rubber, [7] medicine, [8–11] pesticides[12] and fungicides.[13,14] In addition, metal dithiocarbamate complexes are used as a single-source precursor for the preparation of metal sulfide nanoparticles. [15–22] In recent years, dithiocarbamate complexes of zinc and cadmium have been extensively studied because of their important applications. Crystal structures of many $[Zn(dtc)_2]$ and $[Cd(dtc)_2]$ complexes have been reported. [23–30] Most of the $[Zn(dtc)_2]$ complexes and all the [Cd(dtc)₂] exist as centrosymmetric dimer.[23-26] A few complexes, such as bis(N-cyclohexyl-N-methyldithiocarbamato-S,S')zinc(II) and bis(N-isobutyl-Npropyldithiocarbamato-S,S')zinc(II), adopt monomeric structures.[27,28] This reveals that the nature of organic substituent in dithiocarbamate ligand affects the structure of the complexes in solid state. There are no secondary intra/intermolecular bonding interactions observed in most of the complexes. But complexes with functionalized dithiocarbamate exhibit secondary intra-and intermolecular C-H···S, C-H···O, C-H···N and C-H··· π (CS₂M ring) interactions. These interactions result in a variety of structural motifs ranging from polymer, 2D-arrays and 3D network structures.[31] Our aim is to study the effect of functionalization of a phenyl group in dibenzyldithiocarbamate on the structures of complexes in the solid state. In this paper, we present the preparation, spectral and crystal structures of bis(N-benzyl-N-(4-methoxybenzyl)dithiocarbamato-S,S')zinc(II) (1) and bis(N-benzyl-N-(4-chlorobenzyl)dithiocarbamato-S,S')cadmium(II) (2). In addition, the preparation of ZnS and CdS from complexes 1 and 2, respectively, is also reported.

2. Results and discussion

The ligands, *N*-benzyl-*N*-(4-methoxybenzyl)dithiocarbamic acid and *N*-benzyl-*N*-(4chlorobenzyl)dithiocarbamic acid, derived from *N*-benzyl-*N*-(4-methoxy)benzylamine and *N*-benzyl-*N*-(4-chlorobenzyl)amine and carbon disulfide, reacted with $ZnSO_4 \cdot H_2O$ and $Cd(CH_3COO)_2 \cdot 2H_2O$ (1:2 molar ratio), respectively, to form complexes **1** and **2**. Complexes **1** and **2** are colorless and pale yellow, respectively, and are stable in air and soluble in common organic solvents.

2.1. IR spectral studies

The formation of complexes **1** and **2** could be evidenced straightforwardly from the IR and NMR spectra. IR spectra of **1** and **2** show bands at 1479 and 1476 cm⁻¹, respectively, that is typical for the vibrations of the v_{C-N} (thioureide) bond.[32] This band is intermediate between $v_{C=N}$ (1640–1690 cm⁻¹) and v_{C-N} (1250–1350 cm⁻¹), indicating partial double bond character of the v_{C-N} bond.[33] Another band in the region 950–1050 cm⁻¹ is important in deciding the coordination mode of dithiocarbamate.[34] In the case of **1** and **2**, a single band is observed around 1010 cm⁻¹ characteristic for bidentate coordination of dithiocarbamate.

2.2. NMR spectral studies

2.2.1. ¹H NMR spectral studies

Two singlets appearing for 1 (4.98 and 5.03 ppm) and 2 (5.09 and 5.13 ppm) are due to methylene protons of benzyl and substituted benzyl groups. Comparison of methylene

proton chemical shift values reveals that a small upfield shift of methylene proton signal of substituted benzyl is observed due to the presence of electronegative atom (O and Cl) on the *para* position of the phenyl group. The signals observed in the downfield region 6.90–7.39 ppm are due to the aromatic protons of dithiocarbamate ligands.

2.2.2. ¹³C NMR spectral studies

The ¹³C NMR spectra of the complexes **1** and **2** show a signal at 205.6 and 207.1 ppm, respectively. This is ascribed to the carbon of the N–CS₂ moiety.[35] The downfield shift of the NCS₂ chemical shift of complex **2** compared with those of complex **1** may be attributed to an increase in π -bond character or delocalization of π -electron over the NCS₂ moiety contributed by the unshared electron pair in the nitrogen atom.[36] The increase in C–N double bond character of dithiocarbamate ligands in complex **2** is due to the large size of the cadmium ion (Cd²⁺: 92 pm, Zn²⁺: 74 pm) experiencing less steric effect. In complexes **1** and **2**, the carbon signals for methylene groups adjacent to the nitrogen atom appeared in the region 55.0–58.0 ppm. Aromatic carbon signals are observed in the downfield region 114.4–159.7 ppm.

2.3. Single-crystal X-ray studies

ORTEP diagrams of 1 and 2 are shown in Figures 1 and 2. Selected bond distances and bond angles are given in Table 1. From the crystal structure of 1, it is found to exist as a monomer. The unit cell contains four monomeric molecules. This complex represents a rare example of monomeric structure within the zinc(II) bis(dithiocarbamates), which are usually dimeric. The structure of 1 is similar to the other known examples of monomeric zinc(II) dithiocarbamates such as bis(N,N'-dicyclohexyldithiocarbamato-S,S')zinc(II),[38] bis[N-n-butyl-N-(3,5-di-tert-butyl-2-hydroxybenzyl)dithiocarbamato-S,S']zinc(II),[38] bis(dibenzyldithiocarbamato-S,S')zinc(II) [39] and bis(1,2,3,4-tetrahydroquinoline carbodithioato-S,S')zinc(II).[40] The zinc atom in 1 is coordinated by a pair of isobidentate dithiocarbamate ligands with bond distances [Zn-S1 = 2.3305(17) Å, Zn-S2 = 2.3529(18) Å, Zn-S3 = 2.3572(18) Å and Zn-S4 = 2.3448(17) Å)]. The coordination geometry around zinc is distorted tetrahedral geometry as seen in the range of angles from S3-Zn-S4 = 77.96(6)° to S1-Zn-S3 = 131.46(7)°.

In the bis(*N*,*N*-dibenzyldithiocarbamato)zinc(II) complex, there is no intra/intermolecular secondary interactions observed.[39] But in complex 1, the crystal packing is further stabilized by various intra- and intermolecular secondary interactions due to the introduction of methoxy on the phenyl ring of *N*,*N*-dibenzyldithiocarbamate. One hydrogen atom of each methylene participates in intramolecular C–H…S hydrogen bonding interactions and one phenyl ring hydrogen (H12) also forms intramolecular C–H…S interactions (Figure S1) (Table S2). The formation of O2…H7–C7 intermolecular hydrogen bonding interaction results in the 36-membered macrocyclic ring (Figure S2). In addition, the packing is stabilized by edge-to-face C–H… π interaction (C4-H4…Cg (C26-C31)) which results in the formation of a dimer (Figure S3). Another two C–H… π interactions lead to the polymeric chain structure (Figure S4).

The centrosymmetric dinuclear structure of **2** features two tridentate dithiocarbamate ligands and one sulfur atom of each dithiocarbamate ligand bridges two cadmium atoms



Figure 1. ORTEP diagram of complex 1.



Figure 2. ORTEP diagram of complex 2.

1 Bond length		2 Bond length	
Zn1-S4	2.3448 (17)	C15-S1	1.705 (6)
Zn1-S2	2.3529 (18)	C15-S2	1.722 (6)
Zn1-S3	2.3572 (18)	C30-N2	1.322 (8)
S3-C17	1.725 (7)	C30-S3	1.709 (6)
S1-C1	1.731 (7)	C30-S4	1.732 (7)
S4-C17	1.731 (6)	S1-Cd1	2.5827 (17)
S2-C1	1.729 (6)	S2-Cd1	2.5548 (19)
N2-C17	1.337 (8)	S3-Cd1	2.5414 (18)
N1-C1	1.340 (8)	S4-Cd1	2.5840 (16)
	Bond angle	S4-Cd1	2.8504 (16)
S1-Zn1-S4	127.40 (7)		Bond angle
S1-Zn1-S2	78.37 (6)	N1-C15-S1	121.0 (5)
S4-Zn1-S2	127.98 (7)	N1-C15-S2	120.1 (5)
S1-Zn1-S3	131.46 (7)	S1-C15-S2	118.9 (4)
S4-Zn1-S3	77.96 (6)	N2-C30-S3	121.0 (5)
S2-Zn1-S3	121.30 (7)	N2-C30-S4	119.3 (5)
C17-S3-Zn1	82.0 (2)	S3-C30-S4	119.7 (4)
C1-S1-Zn1	82.3 (2)	C15-S1-Cd1	85.1 (2)
C17-S4-Zn1	82.3 (2)	C15-S2-Cd1	85.6 (2)
C1-S2-Zn1	81.7 (2)	C30-S3-Cd1	91.5 (2)
C17-N2-C18	122.7 (5)	C30-S4-Cd1	100.0 (2)
C17-N2-C25	122.4 (5)	C30-S4-Cd1	81.2 (2)
C1-N1-C2	121.5 (5)	Cd1-S4-Cd1	82.28 (5)
C1-N1-C10	123.3 (5)	S3-Cd1-S2	135.63 (6)
C2-N1-C10	115.1 (5)	S3-Cd1-S1	117.66 (6)
N1-C1-S2	121.2 (5)	S2-Cd1-S1	70.15 (5)
N1-C1-S1	121.2 (5)	S3-Cd1-S4	98.41 (6)
S2-C1-S1	117.6 (4)	S2-Cd1-S4	122.62 (6)
N2-C17-S3	121.7 (5)	S1-Cd1-S4	105.29 (6)
N2-C17-S4	120.6 (5)	S3-Cd1-S4	66.70 (5)
S3-C17-S4	117.7 (4)	S2-Cd1-S4	89.87 (5)
		S1-Cd1-S4	155.24 (6)
		S4-Cd1-S4	97.71 (5)

Table 1. Selected bond distances (A°) and angles (°) of complexes 1 and 2.

leading to the formation of a Cd₂S₂ core. The two remaining ligands are coordinated anisobidentately to the cadmium atom. The coordination geometry around each cadmium is defined by S₅, which defines an environment intermediate between trigonal bipyramidal and square pyramidal. Characterization of the distortion from square-pyramidal toward trigonal pyramidal can be found from the τ_5 value.[41] From the τ_5 (0.32) value, the coordination geometry is described as being 32% distortion from the square pyramidal toward the trigonal bipyramid.

No secondary interactions are observed in bis(*N*,*N*-dibenzyldithiocarbamato-S,S') cadmium(II).[25] However, C–H···S, C–H···N and C–H··· π interactions are found in complex **2** (Table S2). Various intramolecular C–H···S (C8-H8B···S1, C1-H1B···S2, C22-H22A···S3, C23-H23A···S4) and C–H···N (C3-H3B···N1) hydrogen bonds are observed (Figures S5 and S6). The C–H··· π (chelate) interactions in metal bis(1,1-ditiolates) have been reported. C–H··· π (chelate) interactions lead to the formation of 1D, 2D and 3D supramolecular assemblies.[42] The C–H··· π (chelate) interaction parameters are defined as *d*, the distance between the ring centroid of the MS₂C ring, and the H atom (2.4–3.6 Å), angle between the perpendicular to the MS₂C ring ($\alpha < 20^{\circ}$) and the C–H vector and

 β vector, the C-H··· π (MS₂C ring) (Scheme 1) angle ($\beta = 110-180^{\circ}$). In **2**, the C-H··· π (chelate) interactions (d = 3.001 Å, $\alpha = 15^{\circ}$, $\beta = 145.28^{\circ}$) run in the opposite direction which results in the polymeric chain (Figure 3). The S···S and C-H···Cl interactions provide a ladder structure (Figures S7 and S8). Additionally, four intramolecular C-H···N interactions are observed.

Comparison of bond parameters of complexes 1 and 2 indicates that M–S and C–S bonds are symmetric in 1 and asymmetric in 2. In both the complexes, the C–S [mean = 1.729 and 2.5657 Å for 1 and 2, respectively] and C–N [43] bond lengths lie approximately midway between values expected for single and double bonds. This confirms that the π -electron density is delocalized over the S₂CN moiety and that these bonds have a partial double bond character.

2.4. Valence bond sum analysis

In the present study, the valence bond sum (VBS) method is used to estimate the effective valence of the metal ion of complexes 1 and 2 from the bond lengths obtained from the



Scheme 1. The bond parameter for C–H··· π (chelate) interactions: d = 2.4-3.6 Å, $\alpha < 20^{\circ}$ and $\beta = 110-180^{\circ}$.



Figure 3. Intermolecular Cg1(chelate)…H–C interactions in complex 2.

X-ray crystal structures calculated using Ok/B and B/Ok procedures.[44,45] The values for **1** (1.948(Ok/B) and 2.09 (B/Ok) and **2** (2.064(Ok/B) and 2.1203 (B/Ok)) confirm the valences to be 2.0 as expected. In the case of complex **2**, the VBS value is slightly greater than the sums for **1**.

2.5. Characterization of zinc sulfide and cadmium sulfide

The phases of the as-prepared ZnS and CdS were studied by powder X-ray diffraction analysis. The X-ray diffraction patterns of as-prepared ZnS and CdS are shown in Figures 4 and 5. The sharp peaks observed in the X-ray diffraction patterns of both samples reveal that the as-prepared metal sulfide is crystalline. The diffraction patterns of ZnS could be indexed to the ZnS wurtzite phase (JCPDS No. 08–8484). The diffraction peaks observed in the XRD pattern of CdS correspond to the reflections of [(100), (002), (101), (102), (110), (103) and (112)] (JCPDS Card No.41–1049) wurtzite CdS.

The morphology of the as-prepared metal sulfides was investigated by SEM. SEM image of ZnS reveals that the morphology of ZnS appears cottony due to the combined appearance of fibrous particles (Figure 6(a)). Figure 6(b) shows that the cadmium sulfide particles are made of nanospheres of uniform size and the nanospheres are coupled to numerous nanoflakes.

UV–Vis absorption spectra of as-prepared ZnS and CdS are shown in Figures S9 and S10. An absorption band observed at 260 nm (4.77eV) is due to the first exciton absorption of ZnS. CdS (Figure S10) shows a weak absorption band at 488 nm (2.54 eV). The large blue shift relative to the bulk ZnS (345 ppm) [46] and CdS (512 nm, 2.42 eV) [47] reveals the existence of a strong quantum confinement effect. The observed photoluminescence peak at 310 and 611 nm for as-prepared ZnS and CdS, respectively, is commonly attributed to the excitonic or band edge emission (Figures S11 and S12).

3. Conclusions

Complexes 1 and 2 were prepared and characterized by IR, NMR and single-crystal Xray analysis. Single-crystal X-ray analysis of 1 and 2 reveals that functionalization of a phenyl group in *N*,*N*-dibenzyldithiocarbamate results in increased aggregation between molecules by various interactions such as C–H···S, C–H···N, C–H···O and C–H··· π (chelate) compared to bis(*N*,*N*-dibenzyldithiocarbamato-S,S')M(II) (M = Zn and Cd). These structures are evident with functionalization of a R group in the dithiocarbamate ligand giving impetus to the systematic study of such supramolecular structures. Complexes 1 and 2 are used as single-source precursor for the preparation of ZnS and CdS, respectively, in the presence of ethylenediamine. UV–Vis absorption spectra of ZnS and CdS indicate blue shift in the absorption spectra due to the quantum size effect.

4. Experimental

4.1. Materials and methods

Commercial reagents and solvents were used without further purification and all experiments were carried out in atmospheric air. Carbon, hydrogen and nitrogen contents



Figure 4. PXRD pattern of as-prepared zinc sulfide.



Figure 5. PXRD pattern of as-prepared cadmium sulfide.

were estimated on a varioMICRO V2.2.O microanalyser. IR spectra were recorded in the 4000–400 cm⁻¹ region as KBr pellets on a thermo scientific NICOLET iS5 spectrophotometer. The NMR spectra were recorded on a Bruker 400/100 MHz spectrometer at room temperature in CDCl₃, using TMS as the internal reference. The wide-angle X-ray diffraction (XRD) was recorded using an inel X-ray diffractometer with CuK_{α} radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM, FEI quanta 200 scanning electron microscope instrument) was used to characterize the morphologies of the samples. UV–vis and fluorescence spectra were recorded on a Perkin-Elmer Lambda 35 UV/vis spectrometer and Perkin-Elmer L555 spectrofluorimeter, respectively.

4.2. X-ray crystallography

Single-crystal X-ray diffraction data for 1 and 2 were recorded on a Xcalibur-3/CCD diffractometer using graphite-monochromated CuK α radiation ($\lambda = 0.71069$ Å) and a Bruker axs kappa apex2 CCD diffractometer using graphite monochromated MoKa radiation ($\lambda = 0.71073$ Å) at an ambient temperature, respectively. The structure was solved by the direct method using SHELXS-97 and refined on F^2 by the full matrix least-squares technique using SHELXL-97 [48] for complex 1. In the case of 2, the structure was solved by the direct method using SIR92 [49] and refined on F^2 by the full matrix least-squares technique using SHELXL-2014/7.[50] Non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. Diagrams for both complexes were prepared using ORTEP and Mercury software.[51] The cif files have been deposited at the Cambridge Crystallographic Data Centre with reference numbers CCDC no. 1061916 and



Figure 6. SEM image of as-prepared (a) zinc sulfide and (b) cadmium sulfide.

1061930 for **1** and **2**, respectively. Details of Crystal data, data collection and refinement parameters for complexes **1** and **2** are provided in Table S1.

4.3. Preparation of complexes

4.3.1. Preparation of N-benzyl-N-4-methoxybenzylamine and N-benzyl-N-(4-chlorobenzyl)amine

Benzylamine (4.6 mmol) and substituted benzaldehydes (4-OCH₃ and 4-Cl) (5.1 mmol) were dissolved in methanol (30 mL) and the solution was stirred for 2 h at room

temperature. The solvent was removed by evaporation. The resulting colorless oil was dissolved in methanol–dichloromethane solvent mixture (1:1, 20 mL) and sodium borohydride (13.8 mmol) was added slowly at 5°C and stirred for 2 h before removal in an ice bath. The reaction mixture was stirred at room temperature for 20 h. After evaporation of the solvent, the resulting viscous liquid was washed with water and dichloromethane was added in order to extract the product. Evaporation of the organic layer gave secondary amine (*N*-benzyl-*N*-(4-methoxybenzyl)amine and *N*-benzyl-*N*-(4-chlorobenzyl)amine) as pale yellow oil, respectively.[52,53]

4.3.2. Preparation of complex 1

N-benzyl-*N*-(4-methoxybenzyl)amine (4.0 mmol) in ethanol was mixed with carbon disulfide (4.0 mmol) under ice cold condition. To the resultant yellow dithiocarbamic acid solution, aqueous solution of $ZnSO_4 \cdot 7H_2O$ (2.0 mmol) was added with constant stirring. The solid which precipitated was washed several times with cold water and then dried.

Yield: 88%, m.p: 120–122°C. IR (KBr, cm⁻¹): $\nu = 1479$ (ν_{C-N}); 1033 (ν_{C-S}). ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 4.98$ (s, 4CH₃O–C₆H₄–CH₂–N); 3.82 (s, 4CH₃O–C₆H₄–CH₂–N); 5.03 (s, C₆H₅–CH₂–N); 6.90–7.39 (aromatic protons). ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 52.4$ (4CH₃O–C₆H₄–CH₂–N); 52.4 (C₆H₅–CH₂–N); *ipso carbon*; 159.7; 114.4–134.6 (Other aromatic carbons); 205.6 (NCS₂). Anal. Calcd. for Chemical Formula: C₃₂H₃₂N₂O₂S₄Zn (%): Elemental Analysis: C, 57.34; H, 4.81; N, 4.18; Found: C, 57.23; H, 4.78; N, 4.11;

4.3.3. Preparation of complex 2

N-benzyl-*N*-(4-chlorobenzyl)amine (4.0 mmol) in ethanol was mixed with carbon disulfide (4.0 mmol) under ice cold condition. To the resultant yellow dithiocarbamic acid solution, aqueous solution of $Cd(CH_3COO)_2$ (2.0 mmol) was added with constant stirring. The solid which precipitated was washed several times with cold water and then dried.

Yield: 79%, m.p: 161–163°C. IR (KBr, cm⁻¹): $\nu = 1476 \ (\nu_{C-N})$; 1001 (ν_{C-S}) ; ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 5.09 \ (s, 4Cl-C_6H_4-CH_2-N)$; 5.13 $(s, C_6H_5-CH_2-N)$; 7.26–7.35 (aromatic protons); ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 57.0 \ (4Cl-C_6H_4-CH_2-N)$; 58.0 $(C_6H_5-CH_2-N)$; 127.9–134.6 (aromatic carbons); 207.1 (NCS₂); Anal. Calcd. for chemical formula: $C_{30}H_{26}CdCl_2N_2S_4$ (%): elemental analysis: C, 49.62; H, 3.61; N, 3.86; Found: C, 49.50; H, 3.52; N, 3.74;

4.4. Preparation of ethylenediamine-capped metal sulfides

4.4.1. Preparation of zinc sulfide

About 0.5 g of bis(*N*-benzyl-*N*-(4-methoxybenzyl)dithiocarbamato-S,S')zinc(II) (1) complex was dissolved in 15 mL of ethylenediamine in a flask and then heated to reflux (117°C) and maintained at this temperature for 2 min. The dirty white precipitate obtained was filtered off and washed with methanol.

4.4.2. Preparation of cadmium sulfide

A method similar to that described for the preparation of zinc sulfide was adopted; however the bis(N-benzyl-N-(4-chlorobenzyl)dithiocarbamato-S,S') cadmium(II) (2) complex was

used instead of complex **1**. The yellow precipitate obtained was filtered off and washed with methanol.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed at 10.1080/17415993.2015.1105226 description of location.

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