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Conformational isomerism of the binuclear *N*,*N*-pentamethylenedithiocarbamate cadmium(II) complex, $[Cd_2\{S_2CN(CH_2)_5\}_4]$ on multinuclear (^{15}N, ^{113}Cd) CP/MAS NMR and single-crystal X-ray diffraction data

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Abstract

Crystalline *N*,*N*-*cyclo*-pentamethylenedithiocarbamate (PmDtc) cadmium(II) complex was prepared and studied by means of ^{15}N, ^{113}Cd CP/MAS NMR spectroscopy and single-crystal X-ray diffraction. The unit cell of the cadmium(II) compound comprises two centrosymmetric isomeric binuclear molecules $[Cd_2\{S_2CN(CH_2)_5\}_4]$, which display structural inequivalence in both ^{15}N and ^{113}Cd NMR and XRD data. There are pairs of the dithiocarbamate ligands exhibiting different structural functions in both isomeric molecules. Each of the terminal ligands is bidentately coordinated to the cadmium atom and forms a planar four-membered chelate ring $[CdS_2C]$; whereas pairs of the tridentate bridging ligands combine two neighbouring cadmium atoms forming an extended eight-membered tricyclic moieties $[Cd_2S_4C_2]$, whose geometry can be approximated by a 'chair' conformation. The structural states of cadmium atoms were characterised by almost axially symmetric ^{113}Cd chemical shift tensors. All experimental ^{15}N resonance lines were assigned to the nitrogen structural sites in both isomeric binuclear molecules.

Keywords: ^{15}N, ^{113}Cd CP/MAS NMR spectroscopy; ^{113}Cd chemical shift anisotropy; Binuclear *N*,*N*-dialkyldithiocarbamate cadmium(II) complexes; Molecular structures; Inorganic eight-membered rings

1. Introduction

The high affinity of cadmium for the sulfhydryl groups in proteins makes it one of the most hazardous ecotoxicants [1–3]. As a consequence, cadmium relatively readily substitutes for zinc incorporated in metalloproteins and blocks zinc-containing enzymes. When taken up into the organism, cadmium accumulates in the liver and kidneys and forms stable complexes with intracellular proteins. The latter circumstance causes the cumulative effect and extremely slow removal of cadmium from the organism. Cadmium (even in extremely low concentrations) is able to trigger some forms of tumors and inhibit the DNA mismatch repair mechanism [4,5]. Therefore, the synthesis and study of complexes that firmly fix cadmium can be important in the context of the search for efficient antidotes for cadmium intoxication [6,7]. It is also worth noting that the ability of cadmium to substitute the metals in the active

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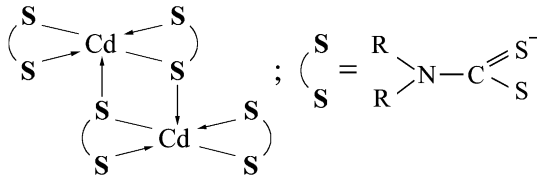
centers of metalloproteins is widely used in biological studies to obtain structural information by ^{113}Cd NMR spectroscopy [8].

All six presently known *N*,*N*-dialkyldithiocarbamate cadmium(II) complexes have the binuclear molecular structures $[Cd_2\{S(S)CNR_2\}_4]$ (R = C_2H_5 [9,10], C_3H_7 [11], *i*-C_3H_7 [12,13], C_4H_9 [14], *i*-C_4H_9 [12,15]; $R_2 = (CH_2)_6$ [16]), in which the mononuclear moieties $[Cd\{S(S)CNR_2\}_2]$ are combined by two additional Cd–S bonds (see Scheme 1).

The discussed structural type of binuclear molecules involves two pairs of dithiocarbamate ligands with terminal chelating and tridentate bridging structural functions. The former Dtc ligands are *S*,*S*′-bidentately coordinated to cadmium and form planar four-membered chelate rings $[CdS_2C]$, whereas the latter combine neighbouring metal atoms into centrosymmetric dimers, forming an extended eight-membered tricyclic moiety $[Cd_2S_4C_2]$, which usually adopts a 'chair' conformation. The only exception is the dibutyldithiocarbamate complex, for which a 'boat' conformation (with a twofold axis) has been established [14]. Each cadmium atom in these complexes is surrounded by five sulphur atoms forming the cadmium coordination polyhedron with a geometry intermediate between tetragonal pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}).

In our previous work [11] we also reported ^{15}N and ^{113}Cd CP/MAS NMR data on the aforementioned dithiocarbamate cadmium(II) complexes. ^{15}N NMR resonance lines have been successfully assigned to the terminal chelating and tridentate bridging ligands in the molecular structures of these cadmium(II) dithiocarbamates. The differences in the isotropic ^{15}N chemical shift values of the dialkyldithiocarbamate ligands have been interpreted invoking the concept of joint manifestation of the mesomeric effect of the =N—C(S)S— groups and the (+) inductive effect of the alkyl substituents.

The present article reports on the preparation, heteronuclear (^{15}N, ^{113}Cd) CP/MAS NMR and single-crystal X-ray diffraction studies of another binuclear cadmium(II) complex with the cyclic *N*,*N*-pentamethylenedithiocarbamate ligand, –S(S)CN$(CH_2)_5$. The structure of this cadmium(II) compound comprises two isomeric centrosymmetric binuclear molecules. Isotropic ^{15}N chemical shift (δ_{iso}) was found to be a sensitive parameter, which correlates with the type of the PmDtc ligands. On this basis all ^{15}N resonance lines have been assigned to the terminal chelating and to the tridentate bridging =N—C(S)S— groups in both binuclear molecules. ^{113}Cd CP/MAS NMR spectra of the prepared cadmium(II) complex show the extended spinning sideband manifolds at moderate spinning (4.6 and 5.5 kHz). ^{113}Cd chemical shift anisotropy (CSA) parameters, δ_{aniso} and η, were calculated from the intensities of spinning sidebands, and these parameters were used to specify a geometry of the neighbouring environment around the central cadmium atoms in the binuclear molecules.



Scheme 1.

2. Experimental

2.1. Materials

Sodium *N*,*N*-pentamethylenedithiocarbamate was obtained by reacting piperidine, $C_5H_{10}NH$ with carbon disulphide, CS_2 in alkaline media [17]. Thermal analysis data showed the presence of the initial crystalline sodium salt as the dihydrated form, $Na\{S_2CN(CH_2)_5\} \cdot 2H_2O$ [17]. The prepared sodium salt was characterised by solid state ^{13}C and ^{15}N CP/MAS NMR (δ, ppm): $Na\{S_2CN(CH_2)_5\} \cdot 2H_2O$ (1:2:2:1): 205.2 (—S_2CN=), 54.6, 53.3 (1:1) (=NCH_2—), 27.4, 27.1 (2:1) (–CH_2–); 135.1 (=N—).

2.2. Synthesis of polycrystalline complex **1**

The binuclear *N*,*N*-*cyclo*-pentamethylenedithiocarbamate cadmium(II) complex $[Cd_2\{S_2CN(CH_2)_5\}_4]$ (**1**) was prepared by mixing aqueous solutions of $Cd(ClO_4)_2 \cdot 6H_2O$

Table 1
Selected crystal data for $[Cd_2\{S_2CN(CH_2)_5\}_4]$

Empirical formula	$C_{24}H_{40}N_4S_8Cd_2$
Fw	865.88
Crystal system	triclinic
Space group	$P\bar{1}$
Crystal shape	prism
Crystal size (mm)	$0.186 \times 0.086 \times 0.078$
Unit cell dimensions	
a (Å)	8.747(1)
b (Å)	12.526(1)
c (Å)	15.963(2)
α (°)	80.567(2)
β (°)	89.917(2)
γ (°)	72.832(2)
V (Å^3)	1646.4(3)
Z	2
D_{calc} (g cm^{-3})	1.747
Temperature (K)	173(1)
μ (Mo Kα) (mm^{-1})	1.822
θ-Range	3.46–28.01
Range of *h*, *k* and *l*	$-11 \rightarrow 10$, $-16 \rightarrow 13$, $-16 \rightarrow 21$
F(000)	872
R_{int}	0.0251
N_{obs}	6291
Criterion of significance	$I > 2\sigma(I)$
N(parameters)	343
Weighting scheme	$w = 1/[s^2(F_o^2) + (0.0498P)^2 + 0.8444P]$, where $P = (F_o^2 + 2F_c^2)/3$
S (goodness-of-fit)	1.030
R_1, wR_2, ($F^2 > 2\sigma(F^2)$)	0.0357, 0.0895
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^3)	0.994, −0.803