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LETTER

A novel square planar Cd(II) with four sulfur donor ligands: crystal structure and ^{113}Cd NMR

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In the course of making models, determining their crystal structures and measuring their ^{113}Cd NMR, both in solution and in the solid state, for the structural and enzymatic sites in horse liver alcohol dehydrogenase [1], we had occasion to make the potassium salt of bis(dimercaptomethylenemalononitrile)Cd(II), $(\text{i-MNT})_2\text{Cd(II)}^{2-}$. Based upon reasonable chemical intuition and most of the known chemistry of Cd(II) and particularly since bis(toluene-2,3-dithiolato)Cd(II)$^{2-}$, $(\text{TDT})_2\text{Cd(I)}^{2-}$, is a tetrahedrally coordinated Cd(II) [2], we expected a tetrahedral four coordinate sulfur bonded Cd(II). In contrast to the 796 ppm deshielded value observed in $(\text{TDT})_2\text{Cd(II)}^{2-}$ [3], we observed an isotropic chemical shift in the solid state at 258 ppm deshielded from the standard, indicative of a mixed oxygen/nitrogen coordination sphere or of an octahedral CdS_6 system. Neither of these are likely with this ligand. In order to gain more insight into this anomalous resonance, we carried out a crystal structure analysis on this compound.

Experimental

The ligand was prepared by modifications of a scheme reported in the literature [4]. The preparation of the complex was carried out as follows. A total of 0.8 g $(CH_3CO_2)_2Cd\cdot 2H_2O$ (MCB) in 20 ml methanol was added to a solution of 1.52 g K_2(i-MNT) in 30 ml methanol and stirred for 20 min. The resultant precipitate was filtered and washed with methanol, air dried, then redissolved into 200 ml water and 25 ml acetone. The yellow needle-like crystals appeared one week later. The crystal was sealed into a thin-wall capillary and mounted on an Enraf-Nonius CAD-4 diffractometer interfaced to a microVAX II to collect data*. The structure was solved and refined by standard techniques [5]. The powder CP/MAS ^{113}Cd NMR spectra were taken on a Bruker WP-200 spectrometer with two different spinning speeds (2.8 and 3.45 kHz) [6]. The isotropic chemical shift was identified at +258 ppm relative to the conventional standard.

An ORTEP drawing with relevant distances and angles is shown in Fig. 1. See also 'Supplementary material'.

The structure can be described as an ionic crystal, wherein the complex anions, $(\text{i-MNT})_2\text{Cd(II)}^{2-}$, are interspersed by two potassium cations and two water molecules of hydration. Space group considerations place Cd^{2+} on a center of symmetry and this in turn demands that the CdS_4 unit must be rigorously planar. However, the $C(CN)_2$ parts of the ligand make an angle of 13.2(2)° with this plane. The shortest Cd–Cd distance is the length of the *c* axis (4.032(1) Å). The average of the bonded Cd–S distances is 2.63 Å, approximately 0.1 Å longer than the expected value of 2.5 Å [7]. This is a factor, but not a major factor, in the anomalously shielded value of the chemical shift (*vide infra*). However, this is in line with the general trend that with longer Cd–X distances, i.e. less covalent bonding, the Cd nucleus is more shielded [8]. The shortest Cd–S distance normal to the CdS_4 plane is 2.956(1) Å, i.e. 0.4–0.5 Å longer than an expected Cd–S distance and 0.3 Å longer than the Cd–S distance observed in the CdS_4 plane. Therefore, the structure gives a planar CdS_4 coordination polyhedron, which has not been previously reported. This interpretation is strongly supported by the ^{113}Cd NMR data (*vide infra*).

The binding manner of the K^+ cation is also interesting. Within a sphere of radius 3.5 Å around K^+, one can find eight electron-rich neighbors including two Cd-bound sulfur atoms, two water oxygen atoms and four cyano group nitrogen atoms. However, none of them is nearer than 2.75 Å to K^+. The K^+ cation seems to be sitting in the center of a cage.

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*Cell data, data collection, and refinement parameters: $a=9.6210(6)$, $b=10.944(1)$, $c=4.032(1)$ Å, $\alpha=94.65(1)$, $\beta=98.23(1)$, $\gamma=75.61(1)$°, volume = 406.6(9) Å^3, $Z=1$, formula = $C_8H_4N_4O_2S_4K_2Cd$, $FW=507.0$ g/mol, $D_m=2.09(2)$ g/cm^3, $D_{calc}=2.07$ g/cm^3, space group = $P\bar{1}$, size of crystal: 0.25×0.14×0.11 mm, range of *hkl* values: $h=0$ to 13, $k=-15$ to 15, $l=-5$ to 5, 2497 reflections measured to $2\theta=60$°, 2053 reflections used to solve and refine by full matrix least-squares, number of variables = 100, final $R=0.034$, weighted $R=0.044$, error of observation of unit weight = 2.395.

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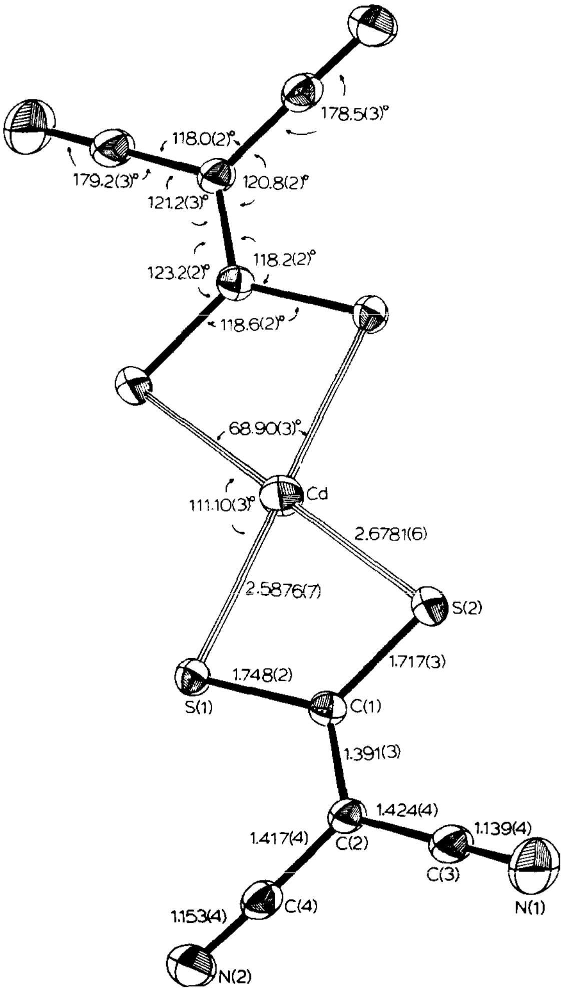

Fig. 1. An ORTEP drawing of an isolated bis(dimercaptomethylenemalononitrile)$_2^{2-}$ ion, with thermal ellipsoids at the 50% probability level. The central Cd atom is on a center of symmetry and, for clarity, distances are shown on one half of the ion and angles are shown on the related half (e.s.d.s are in parentheses).

The powder CP/MAS^{113}Cd NMR spectrum of this compound reveals an axially symmetrical spinning side-band pattern with $\eta = 0.01$, consistent with our description of a planar CdS_4 system. A computer simulation extracted the principal shielding tensor elements as 134, 137 and 504 ppm [6]. The orientation of the principal components of the chemical shielding tensor have been analyzed with a program AUTORAN [9] showing that the unique element, 504 ppm, is indeed along the direction normal to the CdS_4 plane, and the other two elements are in the CdS_4 plane and are approximately pointed toward two of the sulfur atoms with similar chemical environments. Since the magnitude of a tensor element reflects the chemical environment in a plane perpendicular to that element, the tensor element perpendicular to the CdS_4 plane, 504 ppm, represents the contribution to the chemical shielding of the Cd nucleus by the four in-plane sulfur atoms. The planes perpendicular to the other two tensor elements contain only two sulfur atoms and represent much more shielded values, 134 and 137 ppm. Thus, the high anisotropy results in an anomalously shielded isotropic chemical shift of 258 ppm.

An alternative description of the geometry about Cd could be one of a tetragonally elongated octahedron, particularly since CdS_6 compounds have been reported with isotropic chemical shifts of 277 ppm [10] and the 'average' of the short and long Cd–S distance herein of 2.74 Å compares well with octahedral $[Cd(S_2X_3)_3]^{-1}$, $X = P(OR)_2$ or CNR_2. The orientation and magnitude of the chemical shielding tensor elements make this description untenable. In addition, it demonstrates how unreliable the ^{113}Cd isotropic chemical shift is as a geometric probe. An interesting comparison is with $Cd(MNT)_2^{2-}$ in which the Cd^{2+} is in a distorted tetrahedral environment [11]. Its isotropic ^{113}Cd NMR chemical shift is 850 ppm and the principal tensor elements are 521, 979 and 1064 ppm [12].

Therefore, in this case the ^{113}Cd NMR isotropic chemical shift is misleading about the coordination sphere of the metal atom even though the coordinating atoms are correct. Nevertheless, the tensor elements do indicate the correct answer. Hence, in a suitably stressed metal environment, especially the active site of metalloenzymes, the ^{113}Cd NMR could readily be misinterpreted.

Supplementary material

Positional parameters and structural details have been deposited with the Cambridge Data Centre.

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