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The Crystal and Molecular Structure of Bis(thiosemicarbazide)-cadmium(II) Sulfate

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The crystal structure of bis(thiosemicarbazide)-cadmium(II) sulfate has been determined by single crystal X-ray diffraction methods. The crystals are monoclinic with the space group $C2/c$, $Z=8$, and the cell dimensions $a=27.962(14)$ Å; $b=6.564(3)$ Å; $c=15.908(9)$ Å and $\beta=126°6'(6)$. The diffraction data were collected on an automatic four circle diffractometer. The structure was determined from three-dimensional Patterson and Fourier functions.

1915 reflections were used to solve and refine the structure for all non-hydrogen atoms. Final unit weighted and weighted residuals of 0.042 and 0.034, respectively, were obtained.

The asymmetric unit contains two independent formula units. Both cadmium complexes have octahedral configuration with sulfate oxygens taking up axial coordination sites such that sulfate ions function as bridges. The remaining four coordination sites are taken up by two unsymmetric bidentate chelate thiosemicarbazides, in one complex in a *trans* configuration and in the other in a *cis* configuration.

The present crystal structure analysis is part of a study on the chemistry of thiosemicarbazide complexes. For a series of alkyl-substituted thiosemicarbazides potentiometric measurements have led to stability constants for the cadmium(II) complexes.[1] The results show that the mono and bis("thiosemicarbazide")cadmium(II) complexes are formed with stability constants varying significantly for differently substituted thiosemicarbazides. This is not unexpected and the trends have been rationalized semi-quantitatively in terms of the electronegativity of the substituents. Nørlund Christensen and Rasmussen [2] found that the stability of the tris(thiosemicarbazide)cadmium-(II) ion is low and proposed to explain this as a stereochemical change from a tetrahedrally coordinated bis complex to an octahedrally coordinated tris complex. The series of substituted ligands gives tris complexes with stability constants identical within the experimental uncertainty and thus confirms Nørlund Christensen and Rasmussen's proposal. The present structure determination of the bis(thiosemicarbazide)cadmium(II) sulfate was initiated in an attempt to obtain further knowledge on the stereochemistry of the bis complex.

EXPERIMENTAL

Bis(thiosemicarbazide)cadmium(II) sulfate ($Cd(tscH)_2SO_4$) was precipitated by mixing a 0.05 M aqueous solution of cadmium sulfate and a 0.1 M aqueous solution of thiosemicarbazide in a test tube. Crystals suitable for the X-ray structure determination developed within 24 h. Analysis: Calc.: C 6.15; H 2.58; N 21.51; O 16.30; S 24.62. Found: C 6.10; H 2.57; N 21.61; S 24.42.

Preliminary Weissenberg and precession film data for space group determination was obtained using Cu$K\alpha$ radiation. 12 reflections in the region of 2θ from 40.3 to 47.4 were used in least squares refinement of the unit cell dimensions and the orientation matrix. The density of the crystals were measured by flotation in a mixture of $CHBr_3$ and CCl_4.

Intensity data were collected on a Picker FACS 1 diffractometer using Mo$K\alpha$ radiation from a graphite monochromator.

A crystal with the dimensions $0.11 \times 0.11 \times 0.11$ mm^3 was used for the data collection. A total of 2029 symmetry-independent reflections were collected up to a maximum $\sin\theta/\lambda=0.5946$ by the $\theta-2\theta$ scan technique with

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a 1° min^{-1} scan speed. Backgrounds were measured for 20 s on each side of the peak and 3 standard reflections were monitored for every 40 measurements to check for decomposition of the crystal. At the end of the data collection the intensity of the standard reflections had dropped by 14 % and the colour of the crystal had changed from colourless to light yellow. The decrease in intensity of the standard reflections was used to place the data on a uniform scale. The data was corrected for Lorentz and polarization effects but not for absorption.

The X-ray atomic scattering factors used in the calculations [3] were for Cd from Cromer and Mann [4] and for the remaining atoms from *International Tables*.[5] Anomalous dispersion corrections were made for the cadmium and sulfur atoms only.[6]

All computations were performed on an IBM 370/165 computer using a set of crystallografic programs by Stewart *et al.*[3] and for illustrations ORTEP II.[7]

CRYSTAL DATA

Bis(thiosemicarbazide)cadmium(II) sulfate, $C_2H_{10}N_6O_4S_3Cd$, M = 390.8. Monoclinic (*b* unique), $a = 27.962(14)$ Å, $b = 6.564(3)$ Å, $c = 15.908(9)$ Å, $\beta = 126°6'(6)$; $V = 2293.7$ Å^3; $Z = 8$; $d_{obs} = 2.24$ g/cm^3, $d_{calc} = 2.251$ g/cm^3; $F(000) = 1536$; $\mu = 11.99$ cm^{-1}.

Systematically absent reflections: $l = 2n+1$ for $k = 0$ and $h+k = 2n+1$ for all reflections. Possible space groups *Cc* or *C*2/*c* (No. 9, C_s^4 or No. 15, C_{2h}^6).

STRUCTURE DETERMINATION

The statistical distribution of the calculated *E*-values did not indicate whether the compound crystallizes in the centric space group *C*2/*c* with one formula unit in the asymmetric unit or in the acentric *Cc* with two formula units in the asymmetric unit. In the computed Patterson function high density was found on the line $(0,v,\frac{1}{2})$ and in the plane $(u,0,w)$ indicating that the correct space group is *C*2/*c*.

Assuming a general eight fold position for cadmium the fractional coordinates for this atom were found from the Patterson map to be (1/8,1/4,7/8).

The fourier map phased from the Cd atom showed a larger number of peaks than expected and among these six peaks had a density obviously higher than the rest. Four of these peaks were in bonding distance from the Cd atom. Attempts to interpret these peaks as S and N atoms gave Fourier maps without clear

Table 1. Final atomic coordinates in fractions for the heavier atoms in bis(thiosemicarbazide)-cadmium(II) sulfate, standard deviations $\times 10^5$ in parentheses. The general equivalent positions are (x,y,z), $(\bar{x},\bar{y},\bar{z})$, $\bar{x},y,\frac{1}{2}-z)$, $(x,\bar{y},\frac{1}{2}+z)$, $(\frac{1}{2}+x,\frac{1}{2}+y,z)$, $(\frac{1}{2}-x,\frac{1}{2}-y,\bar{z})$, $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$, $(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$.

	x/a	*y/b*	*z/c*
Cd1	0.00000(0)	0.69552(7)	0.25000(0)
C1	0.06239(17)	0.65348(65)	0.12793(29)
N11	0.03701(16)	0.94088(54)	0.19091(28)
N21	0.05080(16)	0.85340(57)	0.12476(28)
N31	0.08112(19)	0.59373(64)	0.07080(30)
S1	0.05516(5)	0.47485(16)	0.19834(8)
Cd2	0.25000(0)	0.25000(0)	0.00000(0)
C2	0.24071(20)	0.13525(70)	0.36338(34)
N12	0.31312(15)	0.96160(57)	0.04402(27)
N22	0.20759(18)	0.66714(62)	0.04198(30)
N32	0.22605(25)	0.27494(79)	0.29027(36)
S2	0.30861(5)	0.43959(21)	0.16990(9)
O1	0.18723(13)	0.10096(55)	0.05472(26)
O2	0.10897(17)	0.15710(53)	0.07931(26)
O3	0.40592(13)	0.22842(48)	0.07807(22)
O4	0.40667(15)	0.58965(48)	0.04726(26)
S3	0.12047(4)	0.10948(15)	0.00151(7)

Table 2. Thermal parameters for the non-hydrogen atoms in $Cd(tscH)_2SO_4$. The temperature factors, U_{ij}, are in unit of $Å^2 \times 10^{-2}$. The estimated standard deviation from the least squares refinement are given in parentheses in unit of the last significant figure in the parameter value.

	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
Cd1	1.93(2)	2.52(3)	2.05(2)	0.00(0)	1.40(2)	0.00(0)
C1	1.59(18)	2.48(20)	1.95(18)	−0.17(16)	1.06(16)	−0.04(16)
N11	2.68(18)	1.89(17)	3.54(19)	−0.20(14)	2.23(16)	−0.21(15)
N21	2.88(18)	2.38(18)	3.10(18)	0.10(15)	2.25(16)	0.44(15)
N31	4.35(22)	3.66(22)	3.30(20)	0.34(18)	3.08(19)	0.31(17)
S1	3.81(6)	1.82(5)	3.06(5)	0.37(4)	2.67(5)	0.36(4)
Cd2	3.19(3)	3.00(3)	3.38(3)	0.22(2)	1.52(2)	−1.13(2)
C2	3.12(23)	2.68(22)	2.97(22)	0.07(18)	2.17(19)	0.43(18)
N12	2.22(17)	2.69(19)	2.50(17)	−0.14(15)	1.26(15)	−0.06(15)
N22	3.08(20)	2.94(21)	3.11(20)	0.93(16)	1.50(17)	−0.07(17)
N32	6.65(33)	4.73(28)	3.63(24)	−1.19(24)	2.78(24)	1.12(21)
S2	2.34(5)	4.26(7)	3.07(6)	0.91(5)	0.44(5)	−1.14(5)
O1	1.62(14)	4.20(20)	3.97(18)	0.68(13)	1.41(14)	1.16(15)
O2	5.48(21)	3.50(18)	3.70(18)	0.27(16)	3.93(17)	0.26(15)
O3	2.16(15)	2.98(16)	2.15(15)	−0.19(12)	0.85(13)	0.90(12)
O4	3.90(18)	2.12(16)	3.97(18)	−0.27(13)	2.36(15)	−0.17(14)
S3	1.74(5)	2.04(5)	1.88(5)	0.26(4)	1.19(4)	0.42(4)

features of the rest of the structure and the R-factor never decreased to less than 0.40. Instead, the six stronger peaks around each Cd-atom were identified as the two pairs of coordinating sulfurs and sulfur in sulfate ions using the space group *Cc*.

From chemical arguments these peaks were separated between the two independent Cd-atoms. The structure factor calculation from two Cd-atoms and six S-atoms gave $R = 0.25$ and the Fourier map phased from this partial structure showed the positions of the rest of the non-hydrogen atoms in the structure. The positional parameters and isotropic temperature factors for all these atoms were varied in a unit weighted full matrix least squares refinement using the 1915 reflections with intensities greater than their standard deviation. Convergence was obtained at $R = 0.087$.

After advice from R. G. Hazell it was realized that this structure could also be described in the space group *C2/c* with the two Cd-atoms in special positions. In the *cis* complex the Cd-atom has the site symmetry of the twofold axis and in the *trans* complex Cd is in the special position (1/4,1/4,0) with a center of symmetry. Full matrix refinement of the atomic parameters, positional and anisotropic temperature factors corresponding to this structure using the 1915 reflections converged rapidly. The weights used in the least squares refinement were of the form $w = \{1 + [(F - 45)/55]^2\}^{-1}$ as this function gave a mean value of $w(F_o - F_c)^2$ that showed little variation with F. For the last refinement cycle no parameter shifted more than 0.6 σ and the average shift was 0.01σ. The corresponding residuals were $R = 0.042$ and $R_w = 0.034$. The position of the hydrogen atoms were not clearly indicated from the final difference Fourier map, therefore, no attempts were made to locate these atoms.

The resulting coordinates are shown in Table 1 while the thermal parameters are listed in Table 2. A list of the observed and calculated structure factors is available from the authors upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of *bis*(thiosemicarbazide)-cadmium(II) sulfate contains two independent sets of complex ions. They both have octahedral coordination with two oxygens from sulfate groups as axial ligands. The chelating thiosemicarbazide groups are coordinating in the

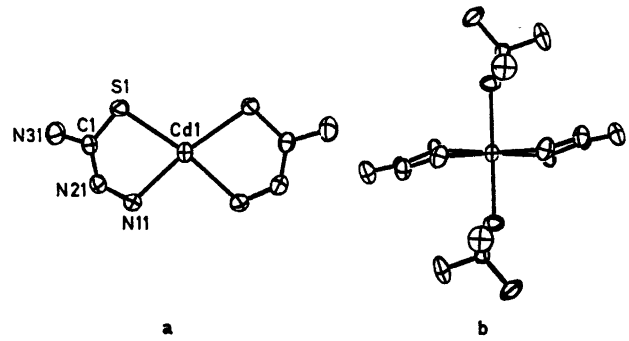

Fig. 1. The *cis*-bis(thiosemicarbazide)cadmium(II) ion viewed perpendicular (a) and parallel (b) to the 2-fold axis of the molecule. The thermal ellipsoids are scaled to include 74 % probability.

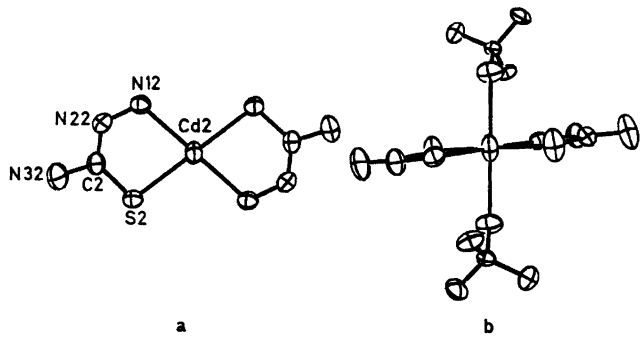

Fig. 2. The *trans*-bis(thiosemicarbazide)cadmium(II) ion viewed parallel (a) and perpendicular (b) to the O – O axis. The molecule is centrosymmetric about the cadmium atom. The thermal ellipsoids are scaled to include 74 % probability.

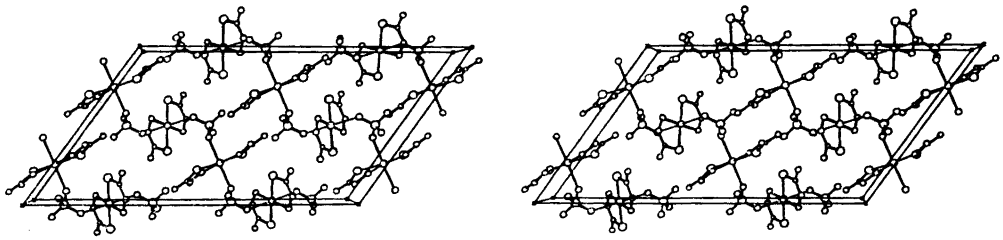

Fig. 3. An ORTEP stereo drawing of a full unit cell as viewed down the *b*-axis (parallel to the 2-fold symmetry axis of the cell).

plane *cis* in one complex (Fig. 1) and *trans* in the other (Fig. 2). Each sulfate group uses two oxygens for coordination, one to each type of cadmium in such a way that chains are formed through the crystal (Fig. 3). Although it was not possible from the final difference Fourier map to locate the hydrogen atoms with certainty, it is indicated from the interatomic distances that the remaining oxygens in the sulfate groups are used for hydrogen bonding to the thiosemicarbazides. In this way the individual chains in the crystal are bound together in a very efficient network which accounts well for the high density and the insolubility of the crystals.

A few examples of structures where two geometric isomers crystallize together are previously reported in the literature.[8–11] Among

Table 3. Bond lengths (in Å) and some angles (in degrees) in $Cd(tscH)_2SO_4$. The estimated standard deviations are given in parentheses in units of the last significant figure of the parameter values.

cis	
Cd1–S1	2.545(2)
Cd1–O3	2.413(3)
Cd1–N11	2.367(5)
S1–C1	1.711(5)
C1–N31	1.336(8)
C1–N21	1.344(6)
N21–N11	1.429(7)
Cd1–S1–C1	97.9(2)
S1–C1–N31	118.7(3)
S1–C1–N21	125.4(4)
C1–N21–N11	121.5(4)
N21–N11–Cd1	112.1(3)
N11–Cd1–S1	77.9(1)
N11–Cd1–N11	94.3(2)
S1–Cd1–S1	110.6(1)
O3–Cd1–O3	169.7(1)
S1–Cd1–N11	170.0(2)
trans	
Cd2–S2	2.514(2)
Cd2–O1	2.525(5)
Cd2–N12	2.367(4)
S2–C2	1.700(5)
C2–N32	1.344(8)
C2–N22	1.339(5)
N22–N12	1.413(6)
Cd2–S2–C2	98.9(2)
S2–C2–N32	117.9(3)
S2–C2–N22	125.5(4)
C2–N22–N12	123.4(4)
N22–N12–Cd2	112.7(2)
N12–Cd2–S2	79.2(1)
Sulfate	
S3–O1	1.484(4)
S3–O2	1.478(5)
S3–O3	1.476(3)
S3–O4	1.477(3)
O1–S3–O2	108.7(2)
O1–S3–O3	109.2(2)
O1–S3–O4	109.3(2)
O2–S3–O3	109.3(2)
O2–S3–O4	109.9(3)
O3–S3–O4	110.3(2)

these is the so-called β-form of bis(thiosemicarbazide)nickel(II) sulfate,[8] which contains planar *cis*- and *trans*-complexes held together by hydrogen bonding between the complex ions and the sulfate ions. Both forms of the nitrate have also been investigated by X-ray structure analysis.[12]

The final bond lengths and angles with their estimated standard deviations for bis(thiosemicarbazide)cadmium(II) sulfate are listed in Table 3. The two independent chelate rings in the asymmetric unit have virtually the same bond distances and angles. The Cd–O bonds are significantly different, with the *cis* complex having the shortest length of 2.413(3) Å compared to 2.525(5) Å in the *trans* complex.

Table 4 gives the bond distances of the metal chelate rings for some thiosemicarbazide complexes for comparison.

Mean planes were calculated for groups of atoms using the coordinates in Table 1. The equations defining these planes and the distance of the atoms to the planes are listed in Table 5.

Both in the *cis* and the *trans* isomers of $Cd(tscH)_2^{2+}$ the thiosemicarbazide skeleton (N–N–C–S) of the chelate rings are planar, with the amide nitrogen a little out of the plane. The *cis* isomer is significantly distorted from an ideal planar arrangement of the ligators and the cadmium ion (Fig. 1). Both a small tetrahedral distortion of the ligating atoms in tscH and a bent configuration is present. This leads to a 0.65 Å displacement of Cd from the plane defined by the atoms in the tscH part of the chelate rings (Table 5).

The S–S distances observed for *cis*-bis(thiosemicarbazide) complexes of nickel and copper are *ca.* 3.1 and 3.4 Å, respectively.[8,12,13] This is considerably shorter than twice the estimated van der Waals radius, 3.7 Å. For such complexes the S–M–S angles are close to 90°. For the *cis*-bis(thiosemicarbazide)cadmium(II) complex the S–S distance is 4.19 Å and S–Cd–S angle is 110.7°. This marked difference between thiosemicarbazide complexes of the transition metals and cadmium illustrates the tendency shown by the former group to maximize the overlap between the empty or partly filled *d*-orbitals and the ligand orbitals.

The number of structures published on cadmium complexes containing sulfur donor atoms are rather limited. They fall in two

Table 4. Some interatomic distances in the thiosemicarbazide ligand in various complexes compared to these found from the present investigation.

	Ref.	M–S	S–C	C–N(3)	C–N(2)	N(2)–N(1)	N(1)–M
cis-Ni(tscH)$_2$(NO$_3$)$_2$	12	2.15 2.15	1.77 1.72	1.29 1.27	1.30 1.31	1.44 1.42	1.95 1.96
trans-Ni(tscH)$_2$(NO$_3$)$_2$	12	2.19	1.71	1.32	1.32	1.43	1.92
trans-Ni(tscH)$_2$(NO$_3$)$_2$.2H$_2$O	20	2.41	1.69	1.35	1.34	1.42	2.05
cis-Ni(tscH)$_2$SO$_4$	8	2.15	1.73	1.32	1.33	1.43	1.93
trans-Ni(tscH)$_2$SO$_4$	8	2.17	1.72	1.32	1.32	1.43	1.92
trans-Ni(tscH)$_2$SO$_4$.3H$_2$O	21	2.16	1.75	1.29	1.33	1.44	1.90
trans-Pt(tscH)$_2$SO$_4$.3H$_2$O	23	2.34	1.74	1.34	1.38	1.46	2.06
cis-Cd(tscH)$_2$SO$_4$	this work	2.55	1.71	1.34	1.34	1.43	2.37
trans-Cd(tscH)$_2$SO$_4$	this work	2.51	1.70	1.34	1.34	1.41	2.37

classes, one containing discrete (usually tetrahedrally coordinated) cadmium(II) ions and another with 6 coordinated Cd(II) obtained as a result of bridge formation of one or more of the ligands. Examples of the former class are for example the structures of bis(thiourea)-cadmium(II) chloride [14] and tetrakis(thiourea)-cadmium(II) tetrakis(thiocyanato)zincate(II).[15] Examples of the second class are more numerous. These are ,*e.g.*, thiourea-cadmium(II) sulfate dihydrate (with sulfate ions and sulfur in thiourea as bridges [16] and bis(ethylenethiourea)cadmium(II) thiocyanate (with two SCN bridges).[17] The structure of tris(thiourea)-cadmium(II) sulfate is described as a binuclear complex built either of distorted octahedrons [18] or of intermediate forms between a square pyramid and a trigonal bipyramid.[19]

The reported cadmium-sulfur bond distances for these complexes are far from being constant. They vary from 2.45 Å in bis(thiourea)-cadmium(II) chloride [14] to 2.73 Å in bis-(ethylenethiourea)cadmium(II) thiocyanate.[17]

Several structures of metal complexes containing thiosemicarbazide (tscH) or similar ligands are reported in the literature: *cis*- and *trans*-Ni(tscH)$_2$(NO$_3$)$_2$,[12] Ni(tscH)$_2$(NO$_3$)$_2$.2H$_2$O,[20] Ni(tscH)$_2$SO$_4$,[8] Ni(tscH)$_2$SO$_4$.3H$_2$O,[21] Ni(tsc)$_2$,[22]

Table 5. Least square planes calculated for some characteristic groups of atoms (marked with an asterisk) in Cd(tscH)$_2$SO$_4$ and the distance from such planes to selected atoms. Symmetry related atoms are marked with a prime. Equation for the planes in direct space is $Px+Qy+Rz=S$.

Cd1	−0.653		Cd1	0.000	
C1 *	0.028		N11 *	−0.134	
N11 *	0.013	I	N11′ *	0.134	II
N21 *	−0.030		S1 *	0.111	
N31	0.126		S1′ *	−0.111	
S1 *	−0.012		C1	−0.417	
Cd2	0.151		Cd2	0.000	
C2 *	0.001		N12 *	0.000	
N12 *	0.001	III	N12′ *	0.000	IV
N22 *	−0.002		S2 *	0.000	
N32	−0.047		S2′ *	0.000	
S2 *	−0.001		C2	0.108	

Plane	P	Q	R	S
I	17.9588	0.8062	3.3266	2.0449
II	9.9814	0.0000	8.5142	2.1285
III	21.6256	−3.6343	−10.6207	−2.4782
IV	22.5094	−3.1967	−11.3321	−2.4363

$Cu(tscH)_2SO_4$,[13] $Pt(tscH)_2SO_4.3H_2O$,[23] $Zn(tscH)Cl_2$,[24] Ag(tscH)Cl,[25] catena-μ-thiocyanato-bis-thiosemicarbazide)silver(I),[26] *cis*- and *trans*-bis(thioacethydroximato)nickel(II),[27,28] acetone thiosemicarbazone zinc(II) chloride,[29] bis-(acetonethiosemicarbazone)nickel(II) chloride monohydrate,[30] bis(thioacethydrazidato)nickel-(II),[31] and bis(ethylenedithiocarbazato)nickel-(II).[32] The crystal structure of the free thio-semicarbazide is also known.[33,34] No crystal structure with Cd^{2+} as the central metal ion with this type of ligands has apparently been reported.

It is an accepted fact that one should be careful, deducing the geometrical structure of labile metal complexes in solution from the structures in the crystalline state. The bis(thio-semicarbazide)cadmium(II) ion is believed [1,2] to have a tetrahedral structure in solution as found indirectly by potentiometric determinations of stability constants while its sulfate salt here is shown to be of octahedral coordination.

As discussed above cadmium complexes can exist in the crystalline state as four as well as six coordinated species. For a long time it has been suspected that this is also the case in solution.[35] Thermochemical studies of cadmium(II) halide complex formation in aqueous and dimethyl sulfoxide solutions have more recently been interpreted in terms of a change in coordination from a supposed hexa-solvate complex to a final tetrahedral tetrahalide complex.[36–38] Moreover, recent X-ray studies of cadmium-aqua and cadmium-iodide solutions have shown that the species $Cd(H_2O)_6^{2+}$ and CdI_4^{2-} indeed are present in the respective solutions and the interatomic distances have been calculated, assuming octahedral and tetrahedral symmetry.[39,40] Thus it is concluded that to a large degree the structure of cadmium complexes is determined by non-bonded interactions between the ligand atoms.

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