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COEXISTENCE OF MONOMERIC AND DIMERIC COMPLEX MOLECULES IN A CRYSTAL: THE CRYSTAL STRUCTURE OF THE β-FORM OF MERCURY(II) N,N-DIISOPROPYLDITHIOCARBAMATE

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The title compound has been found to crystallize from acetone in two modifications. An X-ray diffraction study has revealed that the structure of the β-form belongs to a quite rare type that it contains both monomeric and dimeric complexes. This situation would reflect the coexistence of molecules with different degree of association in solution.

A number of coordination compounds exist with several kinds of molecular association in solution, and some complexes are known to exhibit crystal polymorphism related to the difference of molecular clustering modes.$^{1)}$ In a series of structural investigation of metal complexes with sulfur ligands we found that the title complex crystallizes in two modifications, and have determined the crystal structures of both forms by X-ray diffraction techniques. We wish to report that the equi"molar" monomers and dimers are coexisting in one of these two crystal forms.

Mercury(II) dichloride was added to an aqueous solution of sodium N,N-diisopropyldithiocarbamate, and the precipitates were dissolved in acetone. Two kinds of the crystal of the aimed complex, both being pale yellow pillars, were obtained simultaneously. Seemingly the crystals of both forms, α and β, are somewhat similar to each other in color as well as in external shape, and the presence of the polymorphism was actually found in the course of checking specimens by means of X-ray photographs: the unit cell volume of the β-form was three times that of the α-form. The ratio of occurrence of the α-form to that of the β-form was about 4 to 1. An X-ray structure analysis of the α-form has established that the crystal is composed of isolated monomeric molecules, $Hg(S_2CN\ \underline{i}Pr_2)_2$.$^{2)}$ ($\underline{i}Pr$ = iso-C_3H_7) This paper concerns with the structure of the β-form.

X-Ray diffraction data were taken on a Rigaku four-circle diffractometer with graphite-monochromated CuKα radiation. In total 4005 independent reflections up to 2θ=120° were collected which had F larger than 2.5σ(F). Absorption correction was not applied.

Crystal data: monoclinic, space group A2/a, a=35.06(2), b=9.806(3), c=19.78(2) Å, β=115.7(1)°, U=6130 $Å^3$. Chemical formula unit (as revealed by X-ray structure analysis): $Hg(S_2CN(\underline{i}\text{-}C_3H_7)_2)_2 \cdot Hg_2(S_2CN(\underline{i}\text{-}C_3H_7)_2)_4$. Z=4, D_x=1.80 g cm^{-3}.

Table 1. Fractional atomic coordinates with their estimated standard deviations ($\times 10^4$)

Atom	x	y	z	Beqv[a]	Atom	x	y	z	Beqv[a]
Hg(A)	2500(0)	1260(2)	0(0)	4.4	C(2B)	4680(5)	-2447(19)	5312(9)	2.1
Hg(B)	4592(0)	1001(1)	5006(0)	3.2	C(3B)	4143(6)	961(25)	7182(10)	3.4
S(1A)	3009(2)	1951(6)	1263(2)	3.1	C(4B)	3935(11)	-127(34)	7427(16)	6.7
S(2A)	2363(1)	-146(6)	1018(2)	3.0	C(5B)	4237(10)	2177(34)	7634(14)	6.4
S(1B)	4603(1)	677(5)	6254(2)	2.3	C(6B)	3469(6)	1840(26)	6150(11)	3.7
S(2B)	3834(1)	1631(6)	4975(2)	2.7	C(7B)	3400(8)	3200(32)	5902(16)	5.3
S(3B)	5220(1)	-2286(6)	5855(3)	3.1	C(8B)	3130(9)	765(37)	5630(18)	6.7
S(4B)	4445(1)	-1600(6)	4471(2)	2.8	C(9B)	4681(7)	-3964(24)	6314(13)	3.8
C(1A)	2795(5)	751(19)	1638(8)	2.0	C(10B)	4702(10)	-5503(35)	6215(18)	6.5
C(2A)	3370(6)	1133(20)	2937(9)	2.5	C(11B)	4500(10)	-3541(31)	6857(13)	5.6
C(3A)	3310(7)	2637(26)	3061(11)	4.0	C(12B)	4004(6)	-3583(24)	5160(13)	3.7
C(4A)	3749(6)	825(24)	2788(11)	3.6	C(13B)	3718(6)	-2367(28)	5103(14)	4.5
C(5A)	2770(6)	-518(24)	2679(10)	3.5	C(14B)	3881(8)	-4307(24)	4417(12)	4.1
C(6A)	3044(10)	-1811(32)	2911(16)	6.2	N(A)	2966(4)	517(17)	2374(7)	2.2
C(7A)	2692(8)	76(36)	3323(14)	6.0	N(1B)	3903(5)	1317(17)	6368(8)	2.5
C(1B)	4084(5)	1256(19)	5913(9)	2.2	N(2B)	4464(4)	-3303(17)	5562(8)	2.5

a) Beqv is the equivalent isotropic temperature factor, B/Å^2.

Positions of the mercury atoms were deduced from a Patterson map, and the coordinates of other non-hydrogen atoms were obtained from successive Fourier syntheses. The structure was refined by block-diagonal least-squares method with anisotropic temperature factors to an R value of 0.090. The atomic coordinates are given in Table 1. Estimated errors in positions are: 0.002 Å for Hg, 0.006 Å for S and 0.02-0.04 Å for C and N atoms, respectively. The crystal structure pro-

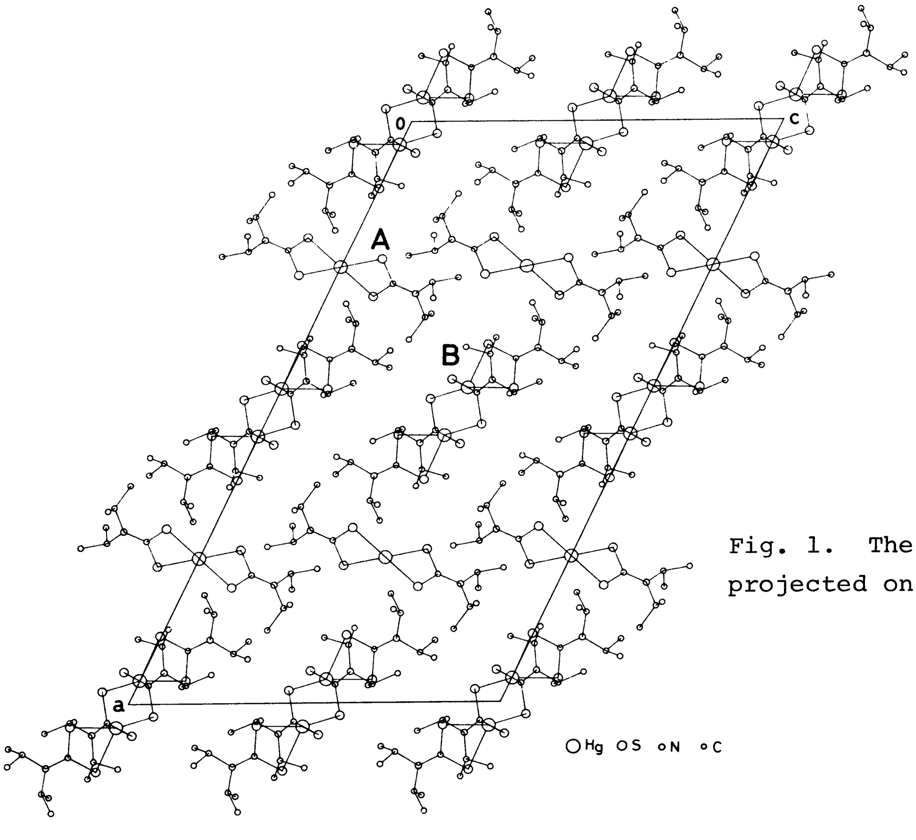

Fig. 1. The crystal structure projected on the (010) plane.

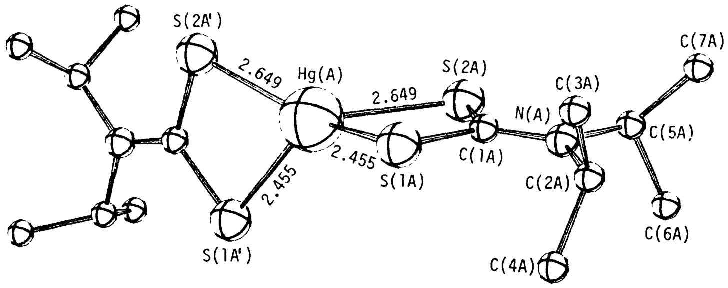

Fig. 2. The geometry of the monomer, molecule A.

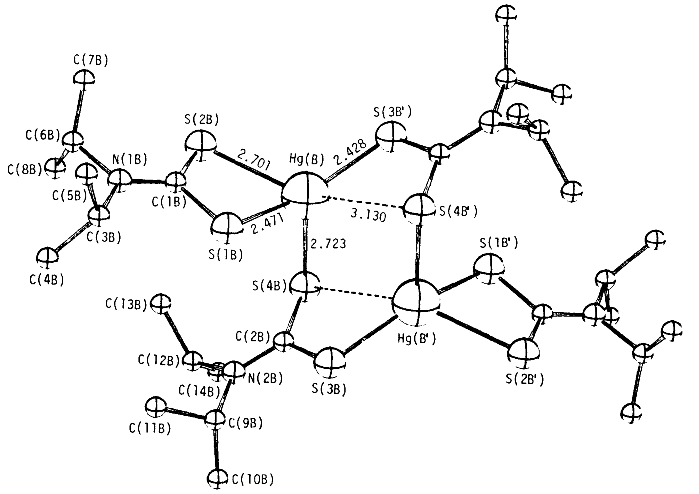

Fig. 3. The geometry of the dimer, molecule B.

jected on the (010) plane is shown in Fig. 1.

The most striking feature of this structure is that monomeric and dimeric complex molecules coexist in the same single crystal. As seen from Fig. 1, the crystal is composed of two kinds of molecules, A and B. The molecular geometry, atomic numbering scheme and Hg-S bond distances (Å) for A and B are illustrated in Figs. 2 and 3, respectively.

The complex A is a monomer. The metal atom lies on a crystallographic two-fold rotation axis, and the complex assumes an exact C_2 symmetry. Two dithiocarbamate ligands are coordinated through sulfur atoms, and the mercury environment is a strongly distorted tetrahedron. This molecular geometry resembles that in the crystal of the α-form.

The complex B is a dimer. The mode of molecular association is essentially the same as that found in a dimeric ethyl analogue, $Hg_2(S_2CNEt_2)_4$. The complex is centrosymmetric. The two dithiocarbamate groups per metal atom serve two independent functions, one acting as a chelating group and the other as a bridging group linking two mercury atoms together to form the dimer. Each mercury atom is surrounded by five sulfur atoms, with four strong and one relatively weak Hg-S bonds.

It is known that the coexistence of monomeric and dimeric dithiocarbamates of heavy metals in organic solvents is rather common,3) and this situation would undoubtedly be reflected in the occurrence of different molecular clustering in crystals of these complexes. In the case of mercury(II) N,N-diethyldithiocarbamate, crystals of monomers and dimers were obtained separately.1) Polymorphism of this type has been observed for other metal complexes also.4) The polymorphism in mercury(II) N,N-diisopropyldithiocarbamate is slightly different, and of the type that the α-form consists of monomers alone while the β-forms contains both monomers and dimers. The chemical significance of the particular structure of the β-form is that the molecules with different degree of association can coexist not only in solution but even in a single crystal. As far as we are aware this is a structure of hitherto unrecorded type.5) It is quite surprizing that we can visualize an association equilibrium in solution through a crystal structure.6)

A remeasurement of the intensity data with MoKα radiation is being planned in order to get a better set of atomic parameters, and a detailed description and discussion of the molecular and crystal structure will be reported later. A part of this work was supported by a Grant-in-Aid for Scientific Research No.354161 from the Ministry of Education, Science and Culture.

References and Notes

1) H. Iwasaki, Acta Crystallogr., B29, 2115 (1973).
2) Crystal data for the α-form: $Hg(S_2CN(\underline{i}-C_3H_7)_2)_2$, monoclinic, space group C2/c, a=19.47, b=8.017, c=14.83 Å, β=119.2°, U=2021 $Å^3$, D_x=1.82 g cm^{-3}, Z=4. The structure will be published elsewhere.
3) Literatures are cited in Ref. 1.
4) For example, compare the following two papers: E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, Acta Crystallogr., 14, 1222 (1961); D. Hall, S. V. Sheat, and T. N. Waters, J. Chem. Soc. (A), 460, 1968.
5) In connection with this it should be added that different types of molecules with similar chemical formulae sometimes appear simultaneously in the same crystal, as in the case of phosphorus "pentachloride" which actually consists of PCl_4 and PCl_6 (R. W. G. Wyckoff, "Crystal Structures", 2nd. ed., Vol. 2, p.170 (1964), Interscience, N.Y.). However, the structural relationship between PCl_4 and PCl_6, for example, is of a quite different and rather complicated type as compared with a simple relation between monomer and dimer in the present case. The former is closer to the case of ordinary molecular complexes or solvent-containing crystals.
6) We are not insisting that any ordering in the arrangement of the two molecular species as seen in the crystal is realized also in solution.

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