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Crystal and molecular structure of hexa(antipyrine)cadmium(II) perchlorate, $[(C_{11}H_{12}ON_2)_6Cd]^{2+}\ [ClO_4]_2^-$

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Crystal structure / Hexa(antipyrine)cadmium(II) perchlorate

Abstract. The crystal and molecular structure of the title compound is reported. Crystals are trigonal with hexagonal axes, space group $P\bar{3}$ with $Z = 1$ in a unit cell of dimensions $a = b = 14.196(7)$ and $c = 9.558(5)$ Å. The structure was solved by the heavy-atom method and refined by the full-matix least-squares method to $R = 0.071$ for 1097 unique reflections. The metal atom of the cation has a regular octahedral configuration and the chlorine atoms of the anions have regular tetrahedral configuration. Both the five- and six-membered rings in the antipyrine are planar having an angle of 113° between the normals to their planes.

Introduction

Structural studies of six-coordinated complexes of transition metals with oxygen atom as the donor atom are interesting. The structural study of one such complex, namely hexa(antipyrine)cadmium(II) perchlorate, is reported herein.

Experimental

Suitable single crystals were kindly supplied by the Department of Chemistry, I.I.T., Madras 600 036. Unit-cell parameters of the crystal were obtained from least-squares refinement of θ values of 25 high-angle reflections.

The crystal data are: $M = 1439.3$, trigonal with hexagonal axes, space group $P\bar{3}$, $a = b = 14.196(7)$, $c = 9.558(5)$ Å, $V = 1669$ Å^3, $Z = 1$, $D_x = 1.43$ g cm^{-3}, $\mu = 0.419$ mm^{-1} and $F(000) = 744$.

A crystal of size $0.25 \times 0.30 \times 0.50$ mm was chosen for study and three-dimensional intensity data were collected at room temperature on an Enraf-

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Nonius single crystal CAD-4 diffractometer with graphite monochromated Mo$K\alpha$ radiation. The data were collected in the $\omega/2\theta$ scan mode at a variable scan speed with a maximum of 60 s per reflection. All reflections (h: -16 to 15, k: 0 to 16, l: 0 to 9) in the range of $2° < 2\theta < 60°$ were measured. 1097 unique reflections with $I > 3\sigma$ (I) were considered as observed. Intensities were corrected for Lorentz and polarization effects but not for absorption. Absence of systematic absences showed the possibility of six space groups: $P3$, $P\bar{3}$, $P312$, $P321$, $P3m1$ and $P31m$. Approximate density measurement showed $Z = 1$. Making use of the molecular symmetry the space group was tentatively fixed as $P\bar{3}$ which later proved to be correct. The cadmium atom lies in the special position 0, 0, 0 with point symmetry $\bar{3}$. One of the oxygen atoms [O(2)] and the chlorine atom of the anions lie in the special positions 1/3, 2/3, Z and 2/3, 1/3, $\bar{Z}$ with point symmetry 3.

The structure was solved by the heavy-atom method and refined by the method of full-matrix least-squares minimizing $\Sigma w(\Delta F)^2$ with SHELX-76 (Sheldrick, 1976), initially with isotropic and then anisotropic thermal parameters. The oxygen atom of the anion lying in the general position [O(3)] shows large thermal motion (see Table 3 for thermal parameters) which may be due to its unrestricted movement. Symmetry restrictions on anisotropic temperature factor parameters for those atoms lying in special positions were applied following the work of Peterse and Palm (1966). The final difference Fourier maps revealed six hydrogen atoms out of a total of twelve to be located. These hydrogen positions were refined once. Location of other hydrogen atoms was not attempted. The final refinement of 174 positional and thermal parameters including the scale factor converged to an R value of 0.071 and R_w of 0.075 with $w = 1.00/[\sigma^2(F_0) + 0.0525|F_0|^2]$. The maximum height in the final difference Fourier map is 0.704 eÅ^{-3} (0.84 Å away from the cadmium atom). The maximum shift/e.s.d. is 0.464.

The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Mann (1968) and the anomalous dispersion correction factors from Cromer and Liberman (1970). The hydrogen scattering factors were taken from Stewart et al. (1965).

Discussion

Fractional atomic coordinates of the nonhydrogen atoms are listed in Table 1. Table 2 contains the fractional atomic coordinates and the isotropic thermal parameters of the hydrogen atoms (revealed by the difference Fourier maps). Table 3 contains the anisotropic thermal parameters for the nonhydrogen atoms. Lists of interatomic distances, bond angles and atom to plane distances are deposited[1]. A chemical drawing of the molecule is shown

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 50745, the names of the authors and the title of the paper.

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Table 1. Fractional atomic coordinates ($\times 10^4$) of the nonhydrogen atoms with estimated standard deviations in parentheses

Atom	x	y	z
Cd	0	0	10000
O(1)	1481(5)	804(5)	8634(8)
C(1)	1969(7)	489(7)	7838(11)
C(2)	1688(8)	−122(8)	6580(11)
C(3)	2603(8)	−127(8)	6124(11)
C(4)	2726(11)	−663(11)	4820(13)
C(5)	4485(9)	483(10)	7089(13)
N(1)	3443(6)	449(7)	6984(9)
N(2)	3057(6)	791(7)	8077(9)
C(6)	3731(7)	1508(8)	9143(10)
C(7)	3515(9)	1128(10)	10508(12)
C(8)	4175(10)	1839(11)	11576(13)
C(9)	4986(10)	2875(10)	11300(13)
C(10)	5165(10)	3213(9)	9930(15)
C(11)	4518(9)	2530(8)	8812(13)
Cl	6667	3333	5004(7)
O(2)	6667	3333	6476(9)
O(3)	6399(10)	4110(8)	4502(10)

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^2$ Å^2) of the hydrogen atoms (revealed by the difference Fourier maps) with estimated standard deviations in parentheses

Atom	Bonded to	x	y	z	U
H(1)	C(2)	80(7)	−58(7)	615(9)	7(3)
H(2)	C(4)	284(7)	−121(7)	520(9)	11(3)
H(3)	C(5)	500(7)	133(7)	709(9)	10(3)
H(4)	C(7)	281(7)	28(7)	1061(9)	6(3)
H(5)	C(8)	393(7)	149(7)	1255(8)	9(3)
H(6)	C(11)	456(6)	278(7)	782(8)	8(2)

in Figure 1 and a schematic plot of Cd(antipyrine) with the atom numbering scheme is presented in Figure 2.

The cadmium and chlorine atoms form alternate parallel layers perpendicular to the c-axis at $Z = 0$ and 1/2 (approximately) respectively.

The metal atom has the regular octahedral configuration with the oxygen atom of six antipyrine molecules coordinated to it. The Cd−O distance observed in the present structure [2.243(7) Å] is less than that reported in the International Tables for X-ray Crystallography, Vol. III (1968) [2.346(2) Å], which shows that the oxygen atom is strongly coordinated with the cadmium atom in the present structure. The O = C bond [1.25(1) Å] is quite normal and

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Table 3. Anisotropic thermal parameters ($\times 10^3$ Å^2) for the nonhydrogen atoms with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd	20(1)	20(1)	34(2)	20(1)	0	0
O(1)	27(3)	42(4)	65(5)	0(4)	13(3)	12(3)
C(1)	31(5)	29(5)	48(6)	9(4)	4(5)	11(4)
C(2)	53(6)	49(6)	36(7)	−2(5)	0(5)	28(5)
C(3)	46(6)	47(6)	38(7)	−5(5)	1(5)	22(5)
C(4)	73(9)	85(9)	51(8)	5(7)	−18(7)	36(8)
C(5)	39(6)	71(8)	72(9)	−11(7)	5(6)	33(6)
N(1)	31(4)	55(5)	46(6)	−10(4)	7(4)	20(4)
N(2)	23(4)	52(5)	41(5)	−11(4)	3(4)	14(4)
C(6)	29(5)	44(6)	46(7)	0(5)	3(6)	22(4)
C(7)	51(7)	74(8)	34(7)	−6(6)	4(5)	28(6)
C(8)	52(7)	91(10)	51(8)	−5(7)	6(6)	31(7)
C(9)	56(7)	64(8)	58(8)	−6(6)	−2(6)	37(7)
C(10)	55(7)	45(7)	97(11)	2(7)	−23(7)	22(6)
C(11)	45(6)	35(6)	62(8)	5(5)	−1(6)	7(5)
Cl	56(2)	56(2)	60(4)	56(2)	0	0
O(2)	29(4)	29(4)	37(7)	29(4)	0	0
O(3)	119(9)	97(8)	92(8)	2(6)	−7(7)	67(7)

The form of the anisotropic temperature factor is
$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$

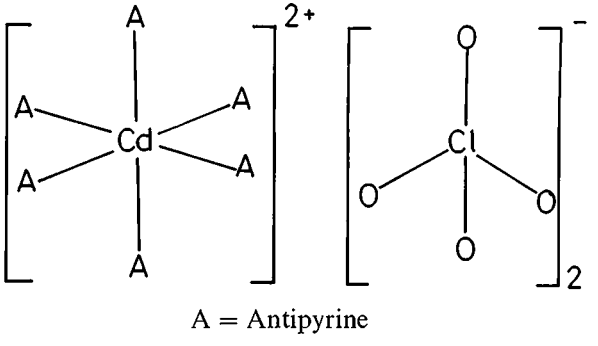

Fig. 1. Chemical representation of the molecule

compares well with that observed in $(C_6H_5)_2Sn\,Cl_2 \cdot OCH\,C_6H_4N(CH_3)_2$ [1.26(2) Å] (Mahadevan et al., 1982).

The phenyl ring is planar to within 0.009(8) Å. The C−C distances in the phenyl ring vary from 1.35(1) to 1.43(2) Å. However, the average C−C distance [1.39(1) Å] is quite normal. The five-membered ring is planar to within 0.023(9) Å. This ring is noncoplanar with the phenyl ring and makes

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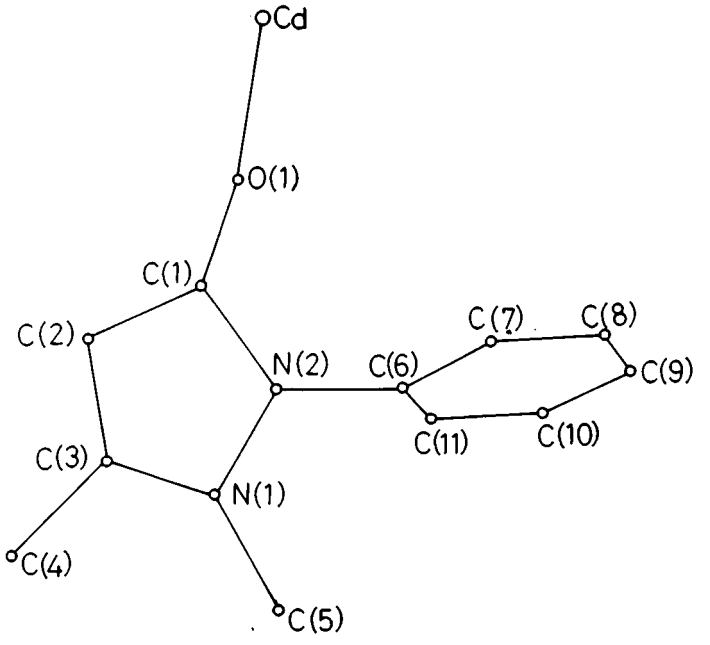

Fig. 2. Schematic plot of Cd(antipyrine)

an angle of 113° with it. C(3) – C(4) and N(1) – C(5) bonds are quite normal. The double bond character of C(2) – C(3) bond is reduced and the bond-multiplicity is spread over the nearby bonds in the same ring.

The chlorine atoms of the anions have a regular tetrahedral configuration with all the Cl – O distances being nearly equal. There is no unusual interaction between the anions and the cation.

References

Cromer, D. T., Liberman, D.: Relativistic calculation of anomalous scattering factors for X-rays. J. Chem. Phys. **53**, 1891 – 1898 (1970)

Cromer, D. T., Mann, J. B.: X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallogr. **A 24**, 321 – 324 (1968)

International Tables for X-ray Crystallography, Vol. III, Birmingham: Kynoch Press (1968)

Mahadevan, C., Seshasayee, M., Kothiwal, A. S.: Dichlorodiphenyl-p-dimethylaminobenzaldehydetin(IV), $C_{21}H_{21}Cl_2$ NO Sn. Cryst. Struct. Commun. **11**, 1725 – 1730 (1982)

Peterse, W. J. A. M., Palm, J. H.: Anisotropic temperature factor of atoms in special positions. Acta Crystallogr. **20**, 147 – 150 (1966)

Sheldrick, G. M.: Program for crystal structure determination (SHELX-76). Univ. of Cambridge, England (1976)

Stewart, R. F., Davidson, E. R., Simpson, W. T.: Coherent X-ray scattering for the hydrogen atom in the hydrogen molecule. J. Chem. Phys. **42**, 3175 – 3187 (1965)

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