希夫碱配合物的研究
Ⅵ.$K[Fe(acacen)(CN)_2]\cdot 2H_2O$ 的合成及晶体结构

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制备了 $K[Fe(acacen)(CN)_2]\cdot 2H_2O$，并测定了晶体结构。单胞中存在两种结构上不同的 $[Fe(acacen)(CN)_2]^-$，空间群为 $P3_1$(# 144)，晶胞参数为：$a=b=11.873(3)$Å，$c=15.002(14)$Å，$V=2808(2)$Å^3，$Z=6$，$D_c=1.44$g/cm^3.

关键词: acacen CN 晶体结构

STUDIES ON SCHIFF BASE COMPLEXES
Ⅵ.SYNTHESIS AND CRYSTAL STRUCTURE OF $K[Fe(acacen)(CN)_2]\cdot 2H_2O$

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Crystals of $K[Fe(acacen)(CN)_2]\cdot H_2O$ were isolated and an X-ray structural examination showed that there were two $[Fe(acacen)(CN)_2]^-$ anions with different structures in the asymmetric unit. Crystal data: space group $P3_1$(# 144), $a=b=11.873(3)$Å, $c=15.002(14)$Å, $V=2808(2)$Å^3, $Z=6$, $D_c=1.44$g/cm^3.

Keywords: acacen CN crystal structure

Introduction

It is well established that the spin state of an Fe(Ⅲ) porphyrin is dependent on the ligand field strength of the axial and equatorial(porphyrin) ligands [1-4]. Generally, the high-spin state arises in five-coordinate ferric porphyrins with a single moderate- or weak-field axial ligand. In contrast, the low-spin state is generally observed for six-coordinate ferric porphyrins having two strong- or moderate-field ligands [1-3]. The investigation on Fe(Ⅲ) complexes with Schiff bases in such area is relatively uncommon. Recently, The μ-oxo complex, $[Fe(Salen)]_2O$ was reported to react with NO and O_2 in solution to produce a solid which appeared by chemical analysis to be $Fe(Salen)NO_3$. When this material was mixed with a secondary amine, an N-nitrosamine formed rapidly and in relatively good yield [5], and

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* Abbreviations: acacen, N,N-bis(acetonylethylidene)ethylenediamine; salen, N,N-bis(salicylidene)ethylenediamine.

N–nitrosamines are carcinogenic materials. In order to proceed with this study, is was necessary to have some detailed information on Fe(Ⅲ) complexes with Schiff bases. Now we report the synthesis and the crystal structure of N,N′–bis(1–acetonylethylidene)ethylenediamine Fe(Ⅲ) complex with two CN^-, $K[Fe(acacen)(CN)_2]\cdot 2H_2O$.

Experimental

synthesis

The ligand acacen was prepared according to the method of McCarthy et al. [6]. A solution containing 150ml of ethanol, 2.02g (0.02mol) of triethylamine, and 5ml of triethylorthorformate was prepared. 2.20g(0.01mol) of acacen was added to this solution with stirring. Under nitrogen flow, 1.60g(0.01mol) of $FeCl_3$ in 20ml of ethanol was added dropwise. After stirring for 2hr at 40–50℃, the reaction mixture was cooled and allow it to stand in refrigerator for two days. The purple crystals of Fe(acacen)Cl was filtered. 0.62g(0.02mol) of Fe(acacen)Cl was dissolved in 150ml of methanol. To this magnetically–stirred solution was added KCN aqueous solution(0.78g, 0.12mol, in 20ml of H_2O). The volume of the solution was reduced to 60ml by slow evaporation. The deep green crystals were collected by filteration.

Instrumentation

A Nicolet R3 / V X–ray diffractometer was used for crystal structure analysis.

Data Collection

A deep green cubic crystal of $K[Fe(acacen)(CN)_2]\cdot 2H_2O$, having approximate dimensions of $0.35\times 0.35\times 0.35mm^3$, was mounted on the end of a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least–squares refinement of the setting angles of carefully centered reflections in the range $28.21<2\theta<29.45°$ corresponded to a cell with dimensions:

$a=11.873(3)$Å, $b=11.873(3)$Å,
$c=15.002(14)$Å, $\gamma=120°$
$V=2808(2)$Å^3

For $Z=6$ and $F.W.=405.35$. The calculated density is 1.44g / cm^3. Based on the systematic absences of:

$0001:\ l=3n\pm 1$

a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P3_1$(#144)

The data were collected at a temperature of 25 ± 1℃, using the ω–2θ scan technique to a maximum 2θ value of 45°. Scans of 0.50° below $K\alpha_1$ to 0.70° above $K\alpha_2$ were made at speeds ranging from 4.88 to 14.65 / min. Stationary crystal, stationary counter background counts were measured at each end of the scan for one–half of the total scan time.

Data Reduction

Of the 5339 reflections collected, 4905 were unique (R_{int} = 0.038). One third of the sphere of reflections($h\ \bar{k}\ l$) was measured, comprising two unique sets of friedel-related data, in order to determine the chirality of the crystal. The linear absorption coefficient for Mo$K\alpha$ radiation is 10.49cm^{-1}. An empirical absorption correction based on azimuthal scans of several intense reflections resulted in transmission factors ranging from 0.85 to 1.00. The data were collected for Lorentz and polarization effects.

Structure Solution and Refinement [7]

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques and those bonded to carbon were included in the structure factor calculation at idealized positions (d_{C-H} = 0.95Å), and were allowed to ride on the atom to which they were bonded. An isotropic group thermal parameter(U_{iso} = 0.076) was refined for all of the hydrogens. Hydrogens bonded to the oxygen atoms of the water molecules were not included in the refinement. The final cycle of full-matrix least-squares refinement was based on 3919 observed reflections($I > 3\sigma(I)$) and 433 variable parameters and converged with final residual values of R = 0.0533, R_w = 0.0698 and quality-of-fit indicator S = 1.05 ($S = \sqrt{[\Sigma(|F_{obs}|-|F_{calc}|)^2 / (N_o - N_v)]}$, where N_o = number of observations and N_v = number of variables.) An analysis of the variance of reflections based on $\sin\theta / \lambda$, magnitude of F and parity class showed no unusual trends. The maximum and minimum peaks on the final difference map corresponded to 0.71 and −0.68e$^-$ / Å^3, respectively, and were located in the vicinity of the iron atoms.

Results and Discussion

The sample crystallizes in the acentric space group $P3_1$(#144), with two anions (Fig.1 and Fig.2), two potassium cations and four water molecules per asymmetric unit. The selection of this space group defines the chirality of the crystal, and was chosen on the basis of a comparison of this refinement with one carried out in the enantiomorphous space group $P3_2$. The significantly better agreement obtained verifies $P3_1$ as the correct space group. The anions pack in spiraling columns along the c-axis of the unit cell (Fig.3). The tunnels formed at the center of these columns contain the potassium ions and waters of hydration, and it is the ionic and hydrogen-bonding interactions between the anions and these cations and solvent molecules which dominate the packing. The potassium ion, K1, has significantly short contacts to atoms O2 of anion 1 (2.745(6)Å), O3 of anion 2 (2.885(6)Å), and water molecules O1 (3.012(6)Å) and O4 of anion 2 (3.167(6)Å). The potassium ion, K2, has short contacts to atoms O4 of anion 2 (2.807(6)Å) and water molecules O5 (2.778(7)Å) ,O7 (2.888(9)Å) and O8 (2.676(9)Å), and a longer contact to atom O3 of anion 2 (2.928(6)Å). There is a 3.121(9)Å contact between atoms K2 and C15, which is probably not an ionic interacion and is more likely a coincidental result of other packing interactions.

Table 1 Bond Lengths(Å)

Fe(1)–O(2)	1.915(6)	Fe(1)–O(1)	1.922(7)
Fe(1)–N(4)	1.921(8)	Fe(1)–N(3)	1.916(7)
Fe(1)–C(2)	1.984(11)	Fe(1)–C(1)	2.011(12)
Fe(2)–O(4)	1.934(6)	Fe(2)–O(3)	1.937(6)
Fe(2)–N(8)	1.919(7)	Fe(2)–N(7)	1.918(7)
Fe(2)–C(16)	2.005(10)	Fe(2)–C(15)	1.989(10)
O(2)–C(10)	1.288(11)	O(1)–C(3)	1.288(11)
O(4)–C(24)	1.300(12)	O(3)–C(17)	1.310(11)
N(2)–C(2)	1.158(14)	N(1)–C(1)	1.134(12)
N(3)–C(6)	1.460(12)	N(3)–C(5)	1.318(12)
N(4)–C(8)	1.303(12)	N(4)–C(7)	1.455(11)
N(6)–C(16)	1.132(13)	N(5)–C(15)	1.138(12)
N(7)–C(20)	1.465(12)	N(7)–C(19)	1.303(12)
N(8)–C(22)	1.294(12)	N(8)–C(21)	1.467(12)
C(3)–C(11)	1.494(14)	C(3)–C(4)	1.402(13)
C(5)–C(12)	1.499(13)	C(4)–C(5)	1.407(13)
C(8)–C(9)	1.424(13)	C(6)–C(7)	1.522(14)
C(9)–C(10)	1.370(13)	C(8)–C(13)	1.504(14)
C(17)–C(18)	1.359(14)	C(10)–C(14)	1.515(12)
C(18)–C(19)	1.422(13)	C(17)–C(25)	1.512(12)
C(20)–C(21)	1.453(15)	C(19)–C(26)	1.515(13)
C(22)–C(27)	1.521(14)	C(22)–C(23)	1.406(14)
C(24)–C(28)	1.530(13)	C(23)–C(24)	1.363(14)

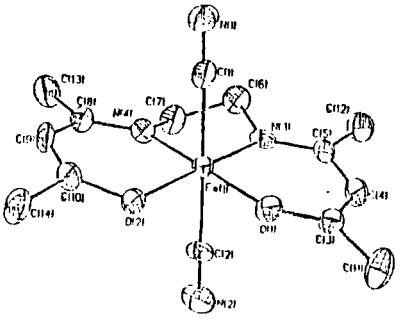

Fig.1 Structural representation of Fe(acacen)$(CN)_2$ (anion 1) with hydrogen atoms omitted (35% probability thermal ellipsoids)

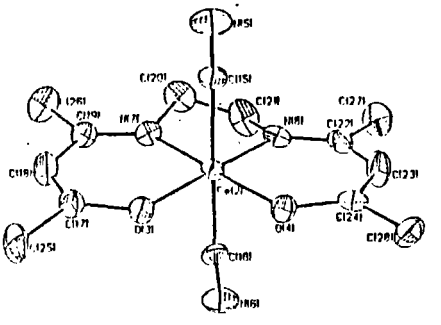

Fig.2 Structural representation of Fe(acacen)$(CN)_2$ (anion 2) with hydrogen atoms omitted (35% probability thermal ellipsoids)

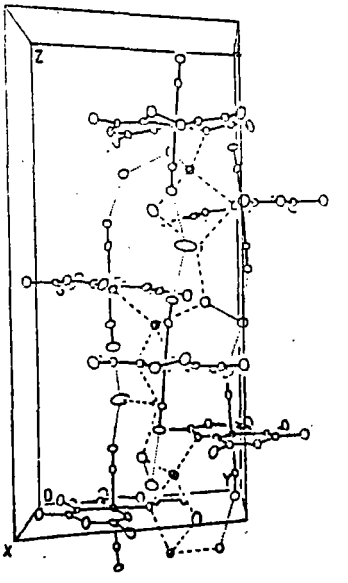

Fig.3 Packing view

Hydrogen bonding occurs between water molecules O5 and O6 (2.78(1)Å). Hydrogen bonding between water molecules and nitrogen atoms of the cyano groups include: O6 to N5 (2.82(1)Å), O6 to N1 (3.13(1)Å, this is a fairly long contact, but is included due to its favorable geometrical arrangement relative to the other two hydrogen bonds to atom O6), O7 to N1 (3.04(1)Å), O8 to N2 (2.81(1)Å) and O8 to N6 (2.80(1) Å).

Table 2　Bond Angles(°)

O(2)–Fe(1)–O(1)	86.0(2)	N(3)–Fe(1)–O(2)	178.0(3)
N(3)–Fe(1)–O(1)	95.0(3)	N(4)–Fe(1)–O(1)	179.8(1)
N(4)–Fe(1)–O(2)	94.1(3)	N(4)–Fe(1)–N(3)	84.9(3)
C(1)–Fe(1)–O(2)	89.2(3)	C(1)–Fe(1)–O(1)	92.1(3)
C(1)–Fe(1)–N(4)	88.1(3)	C(1)–Fe(1)–N(3)	92.4(3)
C(2)–Fe(1)–O(1)	87.6(4)	C(2)–Fe(1)–O(2)	89.7(3)
C(2)–Fe(1)–N(3)	88.7(3)	C(2)–Fe(1)–N(4)	92.3(4)
C(2)–Fe(1)–C(1)	178.9(4)	N(7)–Fe(2)–O(3)	95.9(3)
O(4)–Fe(2)–O(3)	83.2(2)	N(8)–Fe(2)–O(3)	178.5(3)
N(7)–Fe(2)–O(4)	177.5(3)	N(8)–Fe(2)–N(7)	85.4(3)
N(8)–Fe(2)–O(4)	95.5(3)	C(15)–Fe(2)–O(4)	88.3(3)
C(15)–Fe(2)–O(3)	88.8(3)	C(15)–Fe(2)–N(8)	91.9(3)
C(15)–Fe(2)–N(7)	89.4(3)	C(16)–Fe(2)–O(4)	89.6(3)
C(16)–Fe(2)–O(3)	90.9(3)	C(16)–Fe(2)–N(8)	88.3(3)
C(16)–Fe(2)–N(7)	92.7(3)	C(10)–O(2)–Fe(1)	123.2(5)
C(16)–Fe(2)–C(15)	177.9(4)	C(5)–N(3)–Fe(1)	125.8(7)
C(3)–O(1)–Fe(1)	124.0(6)	C(6)–N(3)–C(5)	120.9(8)
C(17)–O(3)–Fe(2)	122.4(2)	C(8)–N(4)–Fe(1)	125.8(7)
C(24)–O(4)–Fe(2)	122.1(6)	C(19)–N(7)–Fe(2)	125.3(6)
C(6)–N(3)–Fe(1)	113.0(6)	C(20)–N(7)–C(19)	121.1(8)
C(7)–N(4)–Fe(1)	111.4(6)	C(22)–N(8)–Fe(2)	126.2(6)
C(8)–N(4)–N(7)	122.6(8)	N(1)–C(1)–Fe(1)	179.1(9)
C(20)–N(7)–Fe(2)	113.0(6)	N(2)–C(2)–Fe(1)	173.8(9)
C(21)–N(8)–Fe(2)	111.3(6)	C(4)–C(3)–O(1)	123.9(9)
C(22)–N(8)–C(21)	121.7(8)	C(11)–C(3)–O(1)	117.0(8)
C(5)–C(4)–C(3)	127.7(8)	C(11)–C(3)–C(4)	118.9(8)
C(12)–C(5)–N(3)	120.9(9)	C(4)–C(5)–N(3)	121.4(8)
C(7)–C(6)–N(3)	106.1(8)	C(12)–C(5)–C(4)	117.6(8)
C(9)–C(8)–N(4)	121.8(9)	C(6)–C(7)–N(4)	107.8(7)
C(13)–C(8)–C(9)	117.9(8)	C(13)–C(8)–N(4)	120.4(9)
C(9)–C(10)–O(2)	125.9(8)	C(10)–C(9)–C(8)	126.0(8)
C(14)–C(10)–C(9)	120.4(8)	C(14)–C(10)–O(2)	113.4(8)
N(5)–C(15)–Fe(2)	176.4(8)	N(6)–C(16)–Fe(2)	174.4(10)
C(25)–C(17)–O(3)	114.1(8)	C(18)–C(17)–O(3)	126.3(8)
C(19)–C(18)–C(17)	127.4(9)	C(25)–C(17)–C(18)	119.5(8)
C(26)–C(19)–N(7)	122.2(9)	C(18)–C(19)–N(7)	122.6(8)
C(21)–C(20)–N(7)	109.5(8)	C(26)–C(19)–C(18)	115.2(8)
C(23)–C(22)–N(8)	121.5(9)	C(20)–C(21)–N(8)	111.6(8)
C(27)–C(22)–C(23)	118.2(9)	C(27)–C(22)–N(8)	120.3(10)
C(23)–C(24)–O(4)	126.4(9)	C(24)–C(23)–C(22)	128.0(9)
C(28)–C(24)–C(23)	120.7(9)	C(28)–C(24)–O(4)	112.8(8)

The two anions in the asymmetric unit have similar conformations, both having essentially non-planar tetradentate "acacen" ligands and two trans cyano groups. However, the non-planarity of "acacen" of anion 1 is significantly more pronounced than for anion 2. The mean deviation from the plane defined by the skeletal atoms of the ligand is 0.14Å for anion 1 and 0.07Å for anion 2. The extended crystal packing in the two directions normal to the *c*-axis is simply close packing the approximately cylindrical columns. The difference in conformation

of the ligands of the two anions is probably due to differences in the steric interactions involved in the packing of these columns.

The more detailed information on bond lengths and bond angles are listed in Table 1 and Table 2, respectively.

The ^1H NMR and magnetic experiments show that K[Fe(acacen)$(CN)_2$] is a low-spin complex, and ν_{CN} exhibits two bands in the IR spectrum as a result of two different anions. We will report these together with the other spectroscopic results in the near future.

Supplementary Material

Full tables of bond distances and angles and calculated factors for K[Fe(acacen)$(CN)_2$] · $2H_2O$ may be obtained from the authors.

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