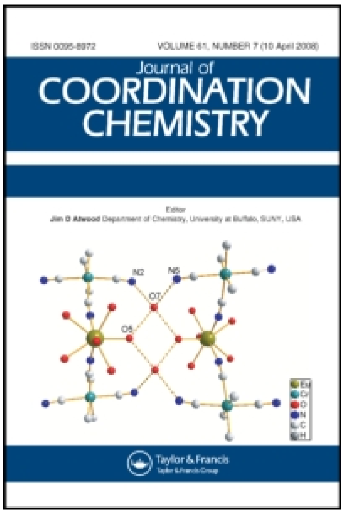

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CRYSTAL STRUCTURE AND MAGNETIC MEASUREMENTS OF *CIS*-DICYANO-*BIS* (1,10-PHENANTHROLINE)IRON(III) SULFATE

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CRYSTAL STRUCTURE AND MAGNETIC MEASUREMENTS OF *CIS*-DICYANO-*BIS* (1,10-PHENANTHROLINE)IRON(III) SULFATE

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The structure of the solvatochromic complex *cis*-dicyano-*bis*(1,10-phenanthroline)iron(III) sulfate dihydrate was determined by X-ray diffraction. The complex crystallized in a compressed octahedral conformation with the cyanide ligands *cis*-bonded. The unit cell contains enantiomeric pairs of the compound with a network of sulfate ions and water molecules stabilized by hydrogen bonding. The magnetic moments of the perchlorate salt dissolved in both water and nonaqueous solvents were probed and found to be in accord with a solvated, low spin $[Fe(III)(phen)_2(CN)_2]^+$ ion, ($\mu_{exp} = 2.0-2.6$ BM, 298 K), showing no dependence on the empirical solvent parameters AN, DN, $E_T(30)$ and π^*.

Keywords: *Cis*-dicyano-*bis*(1,10-phenanthroline)iron(III) (+1); Crystal structure; Enantiomer; Nonaqueous solvent; Magnetic moment

INTRODUCTION

cis-Dicyano-*bis*(1,10-phenanthroline)iron(III)-X^- (X^- = nitrate, perchlorate) (1) has been known for a long time [1] and various investigations were carried out on the molecule (*e.g.*, temperature dependent magnetism in solid state [2], ESR and Mössbauer spectroscopy [3]) No attempts were made to determine its molecular structure, except a vibrational spectroscopy

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study [4], which did not give detailed structural data; the structures of the related compounds [Fe(II)(phen)$_2$(CN)$_2$]·3H$_2$O [5, 6] and [Fe(III)(bipy)$_2$(CN)$_2$]ClO$_4$ [7] are known. **1** and related compounds exhibit interesting coordinative [8, 9] and solvatochromic [10] properties. The latter can be used to indicate and measure Lewis-acidities (Acceptor Numbers of solvents and cations). In contrast to [Fe(II)(phen)$_2$(CN)$_2$], the Fe(III) complex shows a nonlinear, partly reversible solvatochromic behavior, which cannot be explained by a simple donor acceptor interaction [11, 12]. From both an experimental and theoretical point of view, knowledge of the geometry of these compounds allows better understanding of these properties. This encouraged us to determine the crystal structure of [Fe(III)(phen)$_2$(CN)$_2$]SO$_4$. To get additional information on the stability of the dissolved complex toward reduction and ligand exchange, the magnetic moments of the substance were measured in a series of solvents.

EXPERIMENTAL

The complexes **1** were prepared according to literature [1]. Magnetic moments were determined using Evans' method [13]. Proton spectra were recorded on a Bruker AC 250 spectrometer, referenced against an external TMS standard and thermostated to 298.0 ± 0.2 K. Analytical grade solvents were used to make up solutions of the pure solvent and the perchlorate at room temperature respectively, both doped with 1% of the reference compound (*tert*-butanol for water, cyclohexane for all other solvents). Only freshly prepared solutions, deoxygenated by bubbling with nitrogen were used for the NMR experiments.

X-ray Diffraction [14]

Crystals, suitable for structure determination, were obtained by recrystallization of the corresponding nitrate from diluted aqueous sulfuric acid. To prevent loss of solvent, the crystals were immersed in paraffin.

Crystal data together with data collection parameters are given in Table I.

The data were corrected for Lorentz polarization and absorption (SADABS). The structure was solved by the Patterson method using SHELXS97. Structure refinement was carried out with the program SHELXL97 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were inserted in idealized positions and were refined riding on the corresponding atoms.

TABLE I Crystal data and data collection parameters for *cis*-dicyano-*bis*(1,10-phenanthroline)iron(III)-sulfate-dihydrate

Molecular formula	$[Fe(phen)_2(CN)_2]_2SO_4 \cdot 2H_2O$
Crystal size	0.34 × 0.24 × 0.20 mm, brown prism
Crystal system, space group	monoclinic,C2/c
Unit cell dimensions	$a = 15.5667(2)$, $b = 14.1639(1)$, $c = 13.3483(0)$ Å $\alpha = 90$, $\beta = 104.549(1)$, $\gamma = 90°$
Z	4
Diffractometer	Siemens SMART CCD area detector three-circle diffractometer
Temperature	20°C
Wavelength	0.71073 Å (Mo K_α)
θ range for data collection	2.30 to 23.25°
Completeness to $\theta = 23.25°$	99.8%
Reflections collected	2048 ($R_{int} = 0.0187$)
Refinement method	full-matrix least-squares on F^2
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0335$, $wR2 = 0.0948$
Largest diff. peak and hole	0.531 and −0.274 eÅ^{-3}

DISCUSSION

Structure

Figures 1 and 2 represent the molecular structure and the packing diagram respectively (hydrogens omitted).

Atomic coordinates and isotropic displacement parameters are listed in Table II. Selected bond lengths and angles which refer to the core of the complex are summarized in Table III.

The molecule possesses crystallographic two-fold symmetry and exhibits a compressed octahedral structure. The cyanide groups are *cis*-bonded and the two highly planar 1,10-phenanthroline molecules are bidentate ligands forming two five-membered rings with the metal. The unit cell contains enantiomeric pairs of the compound. Figure 2 shows that the molecules are oriented along the *c*-axis of the cell probably due to π-packing interactions between the phenanthroline ligands. In the voids formed by this packing the sulfate anions and the water molecules are found. The coordination sphere around the iron atom is a distorted octahedron with two different Fe–N bond lengths (1.974(2) and 1.990(2) Å). Due to the cell symmetry one cannot distinguish between equatorial and axial planes. The intra-ligand N(1)–Fe–N(11) angle (82.53(8)°) is much smaller than the usual 90° of an octahedron due to steric constraints of the ligand. The angle is, however, within the range usually found for iron-phenanthroline compounds [6, 8]. The increased Fe–C(16) distance (1.922(3)) in comparison to the two unique iron–carbon bond lengths in $[Fe(II)(phen)_2(CN)_2] \cdot 3H_2O$ (1.917(5)

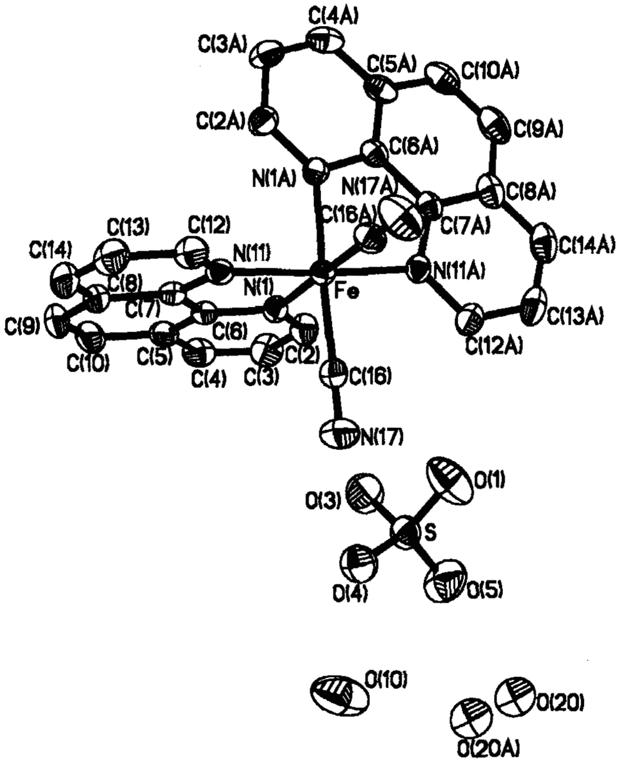

FIGURE 1 ORTEP plot of the $[Fe(phen)_2(CN)_2]^+ - SO_4^{2-} - 2H_2O$ fragment.

and 1.903(6), respectively) points to weaker π-bonding. This results in a slightly decreased C(16)−N(17) bond length (1.141(4)) compared to the two unique ones in the analogous Fe(II) compound (1.149(7) and 1.151(7), respectively). The angle between the *cis*-standing cyanide C atoms with the Fe is 85.98(15)° and therefore smaller than the ideal 90°. This leads to bigger N−Fe−C angles and reflects the distortion of the octahedron. The Fe−C−N angle (178.2(3)°) is close to the ideal 180°. Two oxygen atoms of water molecules were found in the asymmetrical unit, from which one is dispersed over two positions with an occupation factor of 0.5 in each case (O(20)−O(20A)). The distances between the oxygen atoms of the solvent molecules are 2.751 Å (O(10)−O(20), O(10)−O(20A)), the distances to the oxygen atoms of the sulfate anion are 2.528 (O(4)−O(10)), 2.653 (O(5)−O(20)) and 2.814 Å (O(5)−O(20A)). All these distances indicate the presence of hydrogen bonds resulting in a stabilizing network between the sulfate ions and the water molecules.

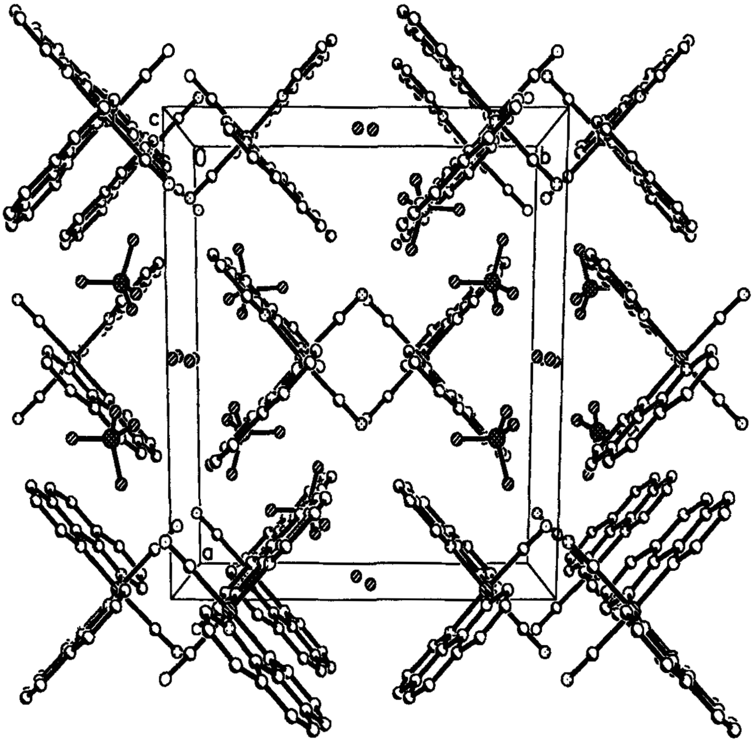

FIGURE 2 Packing diagram of $[Fe(phen)_2(CN)_2]_2SO_4 \cdot 2H_2O$.

Magnetism

Although the observed paramagnetic shifts in the NMR spectra are small due to poor solubility of the complex (about 0.5 – 1 mM), they were reproducible enough to yield magnetic moments with experimental errors less than ± 0.05 BM. The molar susceptibilities, calculated using a revised Evans-equation [16] $\chi_M = (3\Delta\delta)/(4000\pi c)$, were corrected for diamagnetic contributions [17] to give χ_{corr} and the magnetic moments were evaluated by $\mu_{exp} = 2.828(\chi_{corr}T)^{1/2}$ (Tab. IV).

These values are in good agreement with previously reported data for the solid state ($\mu_{exp} = 2.40$ (300 K)[2]). The solvated $[Fe(III)(phen)_2(CN)_2]^+$ ion does not exhibit a solvent dependent variation of magnetic behavior, in accord with its solvatochromic properties. Therefore no correlation with empirical solvent parameters (Acceptor Number, Donor Number, $E_T(30)$, π^*) were found. The slightly increased magnetic moment in the case of acetonitrile and dimethylsulfoxide compared to the solid state can be

TABLE II Atomic coordinates (× 10^4)* and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $[Fe(phen)_2(CN)_2]_2SO_4 \cdot 2H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Fe	0	8332(1)	7500	21(1)
S	−3353(1)	8435(1)	9099(1)	40(1)
N(1)	−937(1)	7342(1)	7253(2)	24(1)
O(1)	−2410(2)	8720(2)	9603(2)	74(1)
C(2)	−1315(2)	6917(2)	7922(2)	33(1)
C(3)	−1959(2)	6226(2)	7622(2)	39(1)
O(3)	−3337(2)	7407(2)	8880(2)	64(1)
O(4)	−3610(2)	8925(2)	8121(2)	55(1)
C(4)	−2224(2)	5959(2)	6607(2)	36(1)
C(5)	−1849(2)	6397(2)	5874(2)	31(1)
O(5)	−3917(2)	8629(2)	9751(2)	78(1)
C(6)	−1210(2)	7088(2)	6239(2)	25(1)
C(7)	−820(2)	7598(2)	5547(2)	25(1)
C(8)	−1084(2)	7418(2)	4483(2)	33(1)
C(9)	−3265(2)	8306(2)	5870(2)	42(1)
C(10)	−2908(2)	8792(2)	5212(2)	40(1)
O(10)	−5000	9904(3)	7500	91(1)
N(11)	−207(1)	8261(1)	5981(2)	24(1)
C(12)	162(2)	8764(2)	5353(2)	33(1)
C(13)	−5078(2)	6364(2)	9283(2)	40(1)
C(14)	−5692(2)	7027(2)	8849(2)	41(1)
C(16)	−868(2)	9324(2)	7307(2)	29(1)
N(17)	−1369(2)	9928(2)	7180(2)	52(1)
O(20)	−4948(4)	9796(5)	10480(4)	82(2)

* The rest of the atom positions are generated by symmetry operation.

TABLE III Selected bond lengths (Å) and angles (°) for $[Fe(phen)_2(CN)_2]_2SO_4 \cdot 2H_2O$

Fe−C(16)	1.922(3)	C(16)−Fe−C(16A)	85.96(15)
Fe−N(11)	1.974(2)	C(16)−Fe−N(1)	91.83(10)
Fe−N(1)	1.990(2)	C(16)−Fe−N(11)	88.35(9)
C(16)−N(17)	1.141(4)	C(16)−Fe−N(1A)	177.34(9)
N(1)−C(6)	1.361(3)	C(16)−Fe−N(11A)	95.91(10)
C(6)−C(7)	1.424(4)	N(11)−Fe−N(1)	82.53(8)
C(7)−N(11)	1.360(3)	Fe−N(1)-C(6)	112.56(16)
O(4)−O(10)	2.528(4)	N(1)−C(6)−C(7)	115.7(2)
O(10)−O(20)	2.751(4)	C(6)−C(7)−N(11)	116.2(2)
		C(7)−N(11)−Fe	112.90(16)
Fe−C(16)−N(17)	178.2	N(1)−C(6)−C(7)−N(11)	1.4(3)

associated with an increased orbital contribution to the magnetic moment [18]. The increased susceptibility in glycol points to small ligand exchange in the Fe(III)-complex where phenanthroline is partly replaced by the alcohol, acting as a chelating ligand, forming $[Fe(III)(phen)_{2-x}(HO - C_2H_4 - OH)_x(CN)_2]^+_{solv}$, which leads to high-spin complexes caused by the decreased strength of the ligand [18]. Moreover this reaction is driven by stabilization

TABLE IV Molar susceptibilities and magnetic moments of $[Fe(III)(phen)_2(CN)_2]ClO_4$ in various solvents

Solvent	χ_M * $10^3/CM^3M^1$	μ_{exp}/B
Water	1.916	2.4
Methanol	1.222	2.0
Ethylene Glycol	2.340	2.6
Nitromethane	1.713	2.3
Nitroethane	1.818	2.3
Acetonitrile	2.055	2.5
Benzonitrile	2.018	2.4
Propylenecarbonate	1.998	2.4
N,N-Dimethylformamide	1.621	2.2
Dimethylsulfoxide	2.141	2.5
n-Propylamine*	1.435	2.1

* 50% (*v*/*v*) in nitromethane to ensure solubility.

of the released strong donor phenanthroline by the large molar excess of the strong acceptor glycol. The absence of the chelate effect in monodentate solvents is the reason for the stability of the complex in strong donors like n-propylamine or dimethylsulfoxide.

In conclusion the investigated crystal structure exihibits a *cis*-structure with respect to the CN-groups like the analogous Fe(II)-complex. Similar to the solvatochromic behavior, no simple relation of the magnetic moments with empirical solvent parameters can be found, suggesting a mutual and therefore complicated electronic interaction between complex, the solvent and possibly the anion.

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