Synthesis, spectroscopic and structural characterization of bis(acetato)tetrakis(imidazole)copper(II): a model complex for DNA binding

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Abstract

The complex bis(acetato)tetrakis(imidazole)copper(II), $[Cu(Im)_4(OAc)_2]$ (**2**), has been prepared by the reaction of excess imidazole with $Cu_2(OAc)_4$. Complex **2** exhibits a magnetic moment of 1.88 BM, consistent with one unpaired electron and the formulation of the complex as a Cu(II) monomer. The frozen-solution ESR spectrum exhibits axial symmetry with $g_{\parallel}$ and $g_{\perp}$ values of 2.221 and 2.040, respectively, and $A_{\parallel}(Cu) = 181 \times 10^{-4}$ cm^{-1}. The $g_{\perp}$ signal and lowest-field component of the $g_{\parallel}$ signal exhibit ^{14}N super-hyperfine structure that consists of nine lines with $A_{\perp}(N) = 15 \times 10^{-4}$ and $A_{\parallel}(N) = 10 \times 10^{-4}$ cm^{-1}. The ESR data are consistent with the tetragonally elongated chromophore $CuN_4...O_2$. Complex **2** crystallizes in the space group *C2/c* with $a = 13.187(2)$, $b = 8.591(1)$, $c = 17.644(2)$ Å, $\beta = 104.13(1)$, $V = 1938.4(5)$ Å^3, $Z = 4$, $D_{calc} = 1.556$ g/cm^3. The relevance of complex **2** to DNA binding of copper(II) imidazole complexes is discussed.

Introduction

Adducts of copper(II) carboxylate dimers are well known for a variety of basic ligands and their preparation, magnetic and spectral properties have been documented [1]. Few monomers with non-halogenated carboxylate ligands, including acetate, are known [2–7]. Several studies have been designed to investigate the factors which influence the adoption of either dinuclear or mononuclear complexes for copper(II) carboxylate adducts [3–6, 8]. Less prevalent are studies of structural types for the monomeric complexes that result from reactions of basic ligands with the dinuclear complexes.

In general, it has been found that by increasing the acidity of the alkyl carboxylate ligands, such as through halogenation of the alkyl groups, and/or by increasing the basicity of the addendant ligands, the tendency towards formation of monomeric complexes increases [1b, 3–6, 8]. Monomeric copper(II) carboxylate adducts with monodentate nitrogen donor ligands for which structural data are available, essentially exist as bis-adducts that contain the CuN_2O_2 chromophore in a *trans* square-planar arrangement [2, 4, 5]. Recently, we reported the structures of bis-adducts of copper(II) acetate with methylimidazole derivatives in which the CuN_2O_2 chromophore exists in a *cis* square-planar arrangement [9].

Our interest in copper(II) carboxylate complexes with imidazole ligands evolves from their biological implications. The imidazole and carboxylate groups are the ligating moieties found in proteins and in many naturally occurring mixed-ligand complexes [10]. In addition, some copper(II) complexes that contain these ligands were found to have a variety of pharmacological activities [11, 12]. For instance, the complex bis(acetato)bis(imidazole)copper(II), $[Cu(OAc)_2(Im)_2]$ (**1**), was recently found to have antitumor activity [11]. Solution ESR parameters were consistent with the formation of a 1:2 complex between **1** and deoxyguanosine (dG) with the Cu(II) in a pseudo-square-planar local environment. These data suggested that **1** may bind to DNA via an interstrand cross-link rather than an intrastrand cross-link as shown for *cis*-diamminedichloroplatinum(II) [13].

The interaction of dimeric copper(II) acetate with imidazole and its methyl derivatives to form **1** and various methylimidazole analogues has been studied previously [2, 9, 14]. While adducts of copper(II) tetraacetate with imidazole, 2-methylimidazole and 1,2-

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dimethylimidazole are monomeric and contain the CuN_2O_2 chromophore in a *trans* or *cis* square-planar arrangement [2, 9], the adduct formed with *N*-methylimidazole is dimeric in which two acetate ions act as monodentate bridging ligands and two act as terminal monodentate ligands [14]. In this structure each copper atom occupies a distorted square pyramidal environment. The nature of the products that result from the reaction of copper(II) acetate with basic ligands are due, at least in part, to the electronic properties of the added bases, though the correlation between these properties and the resulting structures have not been fully assessed.

In our attempt to better understand these correlations and the implications they may have in preparing physiologically active complexes, we have been systematically investigating the roles of reaction conditions and ligand properties on the nature of the adducts formed with copper(II) carboxylates. In order to adequately assess the importance of these variables it is necessary to compare spectroscopic as well as structural data for the complexes studied. The bis-imidazole monomer **1** has been reported as a product of the reaction of imidazole with copper(II) tetraacetate [2], and its antitumor behavior has been reported [11]. Herein we report the synthesis, spectroscopic and X-ray structural characterization of bis(acetato)tetrakis(imidazole)-copper(II) (**2**). For comparison purposes we also report some spectroscopic properties of **1** that were not previously reported. Although the antitumor activity of **2** is not known, **2** is a possible model for DNA binding of Cu(II)–imidazole complexes.

Experimental

Bis(acetato)bis(imidazole)copper(II), $[Cu(OAc)_2(Im)_2]$ (1)

This compound was prepared as described previously [2] from the reaction of imidazole (Im) with $Cu_2(OAc)_4$ in ratio of 4:1. *Anal.* Calc. for $C_{10}H_{14}N_4O_4Cu$: C, 37.8; H, 4.4; N, 17.6; Cu, 20.0. Found: C, 37.9; H, 4.4; N, 17.7; Cu, 20.0%.

Bis(acetato)tetrakis(imidazole)copper(II), $Cu(OAc)_2(Im)_4$ (2)

Method 1. A solution of 3.0 g (4.4 mmol) of imidazole dissolved in 15 ml of methanol was added to 1.0 g (5.5 mmol) of anhydrous copper(II) acetate. The mixture was stirred in an ice bath for 4 h. Anhydrous diethyl ether was added to the blue mixture and stirring was continued at room temperature until a blue–violet precipitate formed. The solution was filtered under reduced pressure and the solid was washed several times with chloroform and anhydrous diethyl ether and air dried.

Method 2. A 0.5 g (2.75 mmol) sample of anhydrous copper(II) acetate was stirred with 0.75 g (11.0 mmol) of imidazole dissolved in 20 ml of chloroform and 3 ml of methanol in an ice bath for 3 h. The blue solution was filtered and left in the hood to evaporate. The blue oily product was dissolved in 75 ml of absolute ethanol. Slow evaporation produced blue–violet crystals. *Anal.* Calc. for $C_{16}H_{22}N_8O_4Cu$: C, 42.3; H, 4.84; N, 24.70; Cu, 14.00. Found: C, 42.24; H, 4.76; N, 24.94; Cu, 14.00%. Carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, TN. Copper was determined volumetrically.

Physical measurements

The room-temperature (298 K) magnetic susceptibility of a powdered sample of **1** and **2** was determined by the Gouy method, with $HgCo(NCS)_4$ as calibrant, and was corrected for diamagnetism with the appropriate Pascal constants. The effective magnetic moment was calculated from the expression: $\mu_{eff}=2.84(\chi T)^{1/2}$. Electronic spectra of methanol solutions were obtained on a Bausch and Lomb spectronic 2000. Nujol mulls sealed between polyethylene sheets were used to obtain IR spectra in the 4000–450 cm^{-1} region with an FTS-7 Bio-Rad SPC 3200 FT-IR spectrometer. Variable-temperature ESR spectra of the powder and methanol/toluene solutions were taken with a Varian E-4 X-band spectrometer equipped with a variable temperature unit and 100 KHz field modulation. Diphenylpicrylhydrazide (DPPH, $g=2.0036$) was used as the calibrating field marker.

X-ray crystallography

Single crystals of **2** were grown by slow evaporation of ethanol solutions. A blue rectangular crystal was selected and cut to give a fragment of dimensions suitable for X-ray analysis. The crystal was coated with Paratone N, a heavy colorless oil obtained from Exxon Corporation. The viscosity of the oil was such that the coated crystal adhered to the end of a glass fiber mounted on a goniometer head. The mounted crystal was quickly placed in a N_2 stream (143 K) on the goniometer and aligned. The unit cell dimensions were determined from least squares refinement of 38 randomly selected high angle ($25<2\theta<45°$) reflections. The orientation matrix and symmetry class were determined by using these reflections. The data were collected on a Siemens R3mV diffractometer between 3.5 and 45° in 2θ. The data were corrected for Lorentz and polarization effects but not for absorption. The absorption coefficient was 11.7 cm^{-1}. The structure was solved by direct methods and successive Fourier syntheses [15]. During the latter refinements, the hydrogen atoms were included at their calculated positions

and were not refined but were allowed to ride along with their bonded atoms during the refinement. The final least-squares cycle of full-matrix refinement gave $R=0.0295$ and $R_w=0.0440$. Other crystallographic and procedural data are given in Table 1. Selected bond distances and angles are presented in Table 2 and atomic positional parameters in Table 3.

Results and discussion

The room-temperature magnetic moments of **1** and **2** in the solid state are 1.90 and 1.88 BM, respectively, and are consistent with the formulation of the complexes as copper(II) monomers with one unpaired electron.

The electronic spectra for **1** and **2** in methanol solutions exhibit one broad asymmetric absorption band at 686 nm ($\epsilon_M=62$) for **1** and 635 nm ($\epsilon_M=60$) for **2**. These spectral parameters are in the range expected for the d–d transition of tetragonally distorted monomeric copper(II) carboxylate adducts [1b]. The spectra lack the charge-transfer band near 370 nm that is characteristic of dimeric copper(II) carboxylate adducts [1, 3]. The position of the band for **1** is comparable with that found for monomeric $Cu(OAc)_2(2\text{-MIm})_2$ and $Cu(OAc)_2(1,2\text{-MIm})_2$ (2-MIm = 2-methylimidazole and 1,2-MIm = 1,2-dimethylimidazole) [9], and other complexes that contain the *trans*- or *cis*-CuN_2O_2 chromophore [1b, 12, 16]. The position of the band in **2** is comparable to that found for monomeric copper(II) carboxylate adducts that contain the CuN_4O_2 chromophore [1b, 6, 16].

The IR absorption bands acetate antisymmetric carboxyl vibration, ν_{as}(COO), for **1** occurs as an intense broad band at 1586 cm^{-1} and that for **2** occurs as a shoulder at 1595 cm^{-1} of an intense broad band centered at 1560 cm^{-1}. The 1560 cm^{-1} band is assigned to absorptions due to imidazole vibrations. The symmetric acetate stretching frequency, ν_s(COO), for **1** occurs at 1418. The position of this band and the small separation between the symmetric and antisymmetric frequencies, $\Delta\nu$(168 cm^{-1}) are consistent with a carboxylate group that acts as an unsymmetrical bidentate ligand [17]. The symmetric stretching frequency, ν_s(COO), for **2** occurs at 1404 cm^{-1}. This value is lower than that of sodium acetate (ν_s(COO) = 1414 cm^{-1}) and is consistent with unidentate coordination of the acetate ligand in **2**.

TABLE 1. Crystal and collection data for $Cu(Im)_4(O_2CCH_3)_2$ (**2**)

Formula	$C_{16}H_{22}N_8O_4Cu$
Formula weight	454.0
Space group	*C2/c*
a (Å)	13.187(2)
b (Å)	8.591(1)
c (Å)	17.644(2)
β (°)	104.13(1)
V (Å^3)	1938.4(5)
Z	4
D_{calc}(g/cm^3)	1.556
Crystal size (mm)	0.55×0.55×0.45
μ (cm^{-1})	11.7
Radiation (monochromated incident beam): λ(Mo Kα) (Å)	0.71073
Temperature (K)	143
Scan method	Wycoff omega
Diffractometer type	Siemens R3mV
Data collection, 2θ range (°)	3.5<2θ<55
No. unique data; total with $F_o>4\sigma(F_o)$	2212; 1955
No. parameters refined	133
R[a]	0.0295
R_w[b]	0.0440
GOF	1.46
Largest and mean Δ/σ	0.001, 0.000
Largest peak (e/Å^3)	0.33

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^{1/2}$, $w=1/(\sigma^2(F_o)+0.0004(F_o)^2)$.

TABLE 2. Bond distances (Å) and bond angles for $Cu(Im)_4(OAc)_2$

Bond distances (Å)			
Cu–N(1)	2.047 (2)	Cu–N(3)	1.977 (1)
C(7)–C(8)	1.514 (3)	C(7)–O(2)	1.261 (2)
C(7)–O(1)	1.263 (2)	Cu···O(2)	2.649
Bond angles (°)			
N(1)–Cu–N(3)	89.1(1)	C(8)–C(7)–O(2)	118.1(2)
C(8)–C(7)–O(1)	119.1(2)	O(2)–C(7)–O(1)	122.8(2)

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for $Cu(Im)_4(OAc)_2$

	x	*y*	*z*	U_{eq}[a]
Cu	0	0	5000	16(1)
N(1)	−658(1)	1557(2)	5617(1)	16(1)
N(2)	−1669(1)	3433(2)	5867(1)	18(1)
N(3)	−181(1)	1535(2)	4143(1)	15(1)
N(4)	−925(1)	2936(2)	3116(1)	17(1)
C(1)	−1217(1)	2800(2)	5338(1)	17(1)
C(2)	−758(2)	1404(2)	6379(1)	24(1)
C(3)	−1377(2)	2555(2)	6536(1)	24(1)
C(4)	−984(1)	1636(2)	3518(1)	16(1)
C(5)	−41(1)	3719(2)	3492(1)	20(1)
C(6)	420(1)	2844(2)	4126(1)	18(1)
C(7)	2210(1)	1722(2)	6226(1)	17(1)
C(8)	2037(2)	3465(2)	6190(1)	29(1)
O(2)	1940(1)	958(1)	5599(1)	19(1)
O(1)	2612(1)	1094(2)	6878(1)	22(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The X-band ESR spectrum of **1** at 77 K has been reported [11] and exhibits resolved structure with $g_{\parallel} > g_{\perp}$. These features are consistent with a tetragonally elongated structure [18]. The $g_{\perp}$ region of the spectrum exhibits ^{14}N super-hyperfine structure that consists of five lines. This splitting is attributed to the presence of two nitrogen atoms in the plane of the copper(II) ion. When **1** was reacted with two equiv. of deoxyguanosine (dG), the ESR spectrum of the complex was altered such that it now consists of nine well-defined lines in the $g_{\perp}$ region that were attributed to ^{14}N super-hyperfine structure. The $g_{\parallel}$ value for the dG-copper species is lower than that of **1** while $A_{\parallel}$ for the dG complex is higher than that of **1**. It was concluded that two dG ligands coordinated to **1** via their imidazole nitrogen atoms to form a CuN_4 or $CuN_4...O_2$ chromophore.

The frozen-solution ESR spectrum of **2** is shown in Fig. 1 and exhibits resolved structure with $g_{\parallel} = 2.221$, $g_{\perp} = 2.040$ and $A_{\parallel} = 181 \times 10^{-4}$ cm^{-1}. The $g_{\perp}$ signal and the lowest-field component of the $g_{\parallel}$ signal exhibit ^{14}N super-hyperfine structure that consists of nine lines with $A_{\perp}(N) = 15 \times 10^{-4}$ cm^{-1} and $A_{\parallel}(N) = 10 \times 10^{-4}$ cm^{-1}. The nine-line pattern is attributed to the interaction of the unpaired electron with four imidazole nitrogen atoms in the plane of the copper(II) ion. The room-temperature solution ESR spectrum of **2** provides the parameters $A_o = 65 \times 10^{-4}$ cm^{-1} and $g_o = 2.122$. The polycrystalline room-temperature ESR spectrum does not exhibit hyperfine splitting, but does provide $g_{\parallel}$ and $g_{\perp}$ values of 2.230 and 2.050, respectively. The spectral parameters are characteristic of tetragonally elongated monomeric copper(II) complexes with $d_{x^2-y^2}$ ground state [18] with $CuN_4...O_2$ chromophores [6, 16, 19] or CuN_4 chromophores [20]. The spectral data are consistent with the formulation of **2** as a tetrakis-imidazole complex. This formulation is verified by a single crystal X-ray structural analysis (*vide infra*).

Molecular structure

The structure of **2** was confirmed by single crystal X-ray analysis. The molecule sits on a crystallographic inversion center with Cu located on the special position $(0,0,\frac{1}{2})$; thus, the asymmetric unit consists of one-half of one molecule. The structure of the complex is shown in Fig. 2 and indicates that the Cu ion resides in a distorted octahedral environment that consists of four imidazole nitrogen atoms in a plane with two carboxylate oxygen atoms in a *trans* disposition along a vector that is nearly perpendicular to the plane of the imidazole nitrogen atoms. As expected for a Cu(II) ion in an approximate octahedral environment, tetragonal distortion occurs that leads to long Cu–O interactions at 2.649 Å. The two imidazole rings that are *trans* to each other lie in the same plane whereas the two imidazole rings that are *cis* to a given ring lie in a plane that is essentially perpendicular (92.5°) to that of the reference imidazole ring. The plane of the acetate group is canted by 61.4° from the O–Cu–O vector such that the acetate groups are folded over two of the imidazole ligands. The Cu–N distance for these imidazole ligands is 2.047(2) Å, whereas the Cu–N distance for the two non-eclipsed imidazole ligands is 1.977(1) Å.

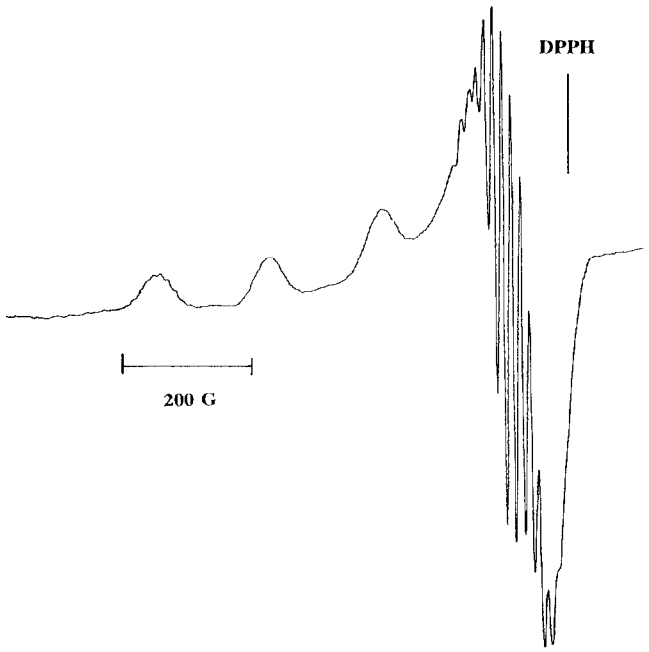

Fig. 1. X-band frozen-solution ESR spectrum of **2**.

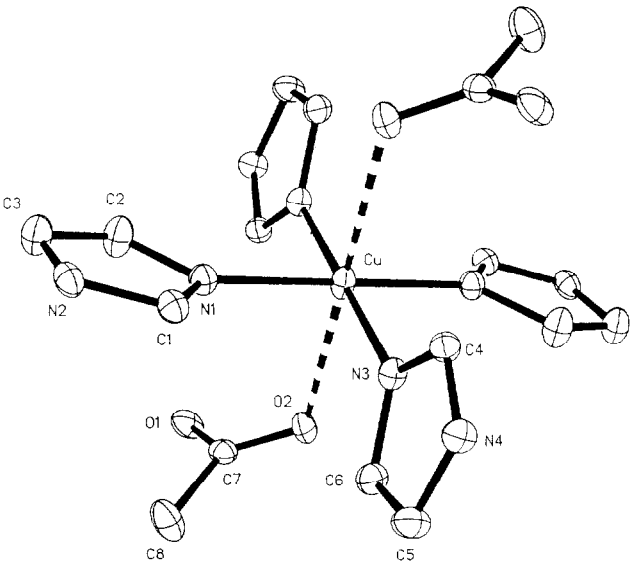

Fig. 2. ORTEP drawing of $Cu(C_3H_4N_2)_4(O_2CCH_3)_2$, showing 50% probability thermal ellipsoids.

One noticeable feature of the structure is that though one carboxylate oxygen atom may be considered to be weakly coordinated to the Cu, the two acetate C–O distances are essentially the same. This probably results from the fact that though one carboxylate oxygen atom O(2) interacts weakly with the Cu, as shown in Fig. 3, the other carboxylate oxygen atom O(1) is heavily involved in hydrogen bonding to the H–N of an imidazole ligand of a neighboring molecule. The O(1)···H distance is 1.751 Å. The donor–acceptor separation, O(1)···N, is 2.670 Å. As the partial network shown in Fig. 3 indicates, O(1) is also 2.573 Å from the hydrogen atom of a H–N of a second neighboring molecule. Interestingly, the acetate oxygen atom O(2) that exhibits weak interaction with the Cu atom also exhibits weak hydrogen bonding interaction (1.950 Å) with H–N of a neighboring molecule. In this instance, the donor acceptor separation, O(2)···N, is 2.805 Å.

Conclusions

The results of this study are consistent with our previous studies that show a preference for monomer formation over dimer formation in copper(II) carboxylate adducts with imidazoles and other strong basic ligands [6, 9, 21]. It is also demonstrated that monomeric adducts of copper(II) carboxylates exist in a variety of structures, even when the added bases are of the same homologous series, such as imidazole derivatives [6, 9, 21]. Although steric effects of the addendant ligands added to the dimers play a less important role than electronic effects in the adoption one of the bis or tetrakis structures [3, 4, 6, 9, 21], the results of this study demonstrate, in part, the role of steric demands of the addendant ligands in affecting the structural properties of monomeric copper(II) carboxylate adducts. The less sterically demanding ligand imidazole forms the *trans* bis-adduct and the tetrakis-adduct with copper(II) acetate, whereas the more sterically hindered ligands 2-methylimidazole and 1,2-dimethylimidazole form the *cis* monomeric bis-adducts with copper(II) acetate, even when excess amounts of ligands are used [9]. It is not clear at this time what role hydrogen bonding interactions such as those depicted for **2** in Fig. 3 play in determining the solid state structures.

The results of this study and those of Tamura *et al.* [11] suggest that bis-imidazole complexes might interact with DNA via an interstrand crosslink rather than an intrastrand cross-link as observed for *cis*-diamminedichloroplatinum(II) [13]. The structure of the monomeric copper(II) complexes may be important in determining whether interstrand or intrastrand cross-linking is the viable mode of interaction of monomeric copper(II) complexes with DNA. We are currently investigating this correlation. To our knowledge this is the first X-ray structure of a tetrakis-adduct of copper(II) carboxylates where the alkyl groups of the carboxylate ligand are not halogenated.

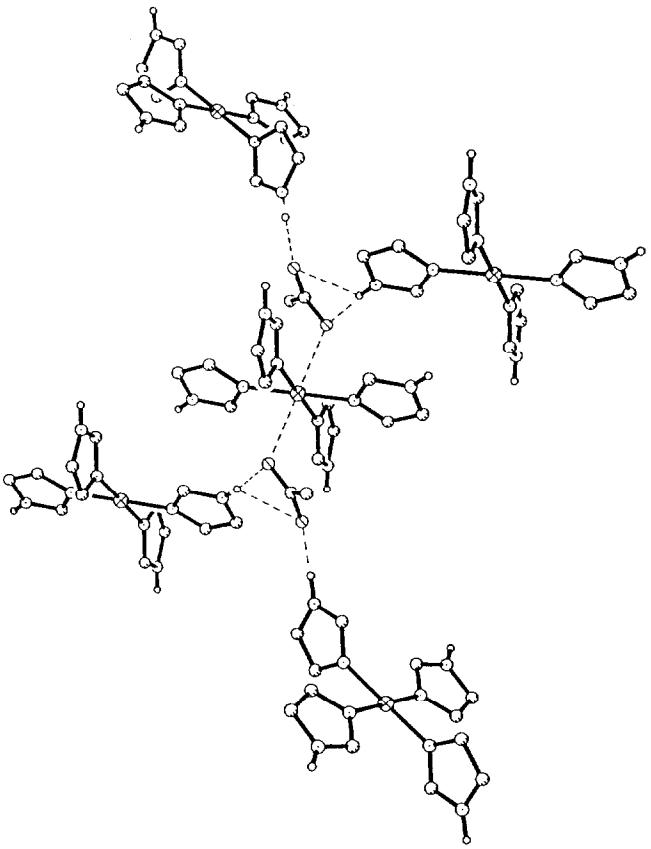

Fig. 3. Diagram illustrating the intermolecular hydrogen bonds between molecules of **2**.

Supplementary material

Complete tables of bond lengths and angles, anisotropic thermal parameters, and observed and calculated structure factors are available from the authors on request.

Acknowledgements

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