Crystal and Molecular Structure of [N,N′-(3,3′-Dipropylmethylamine)bis-(Salicylideneiminato)Iron(II)]

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The crystal structure of [N,N′-(3,3′-Dipropylmethylamine)bis(Salicylideneiminato)Iron(II)], [Fe(SALMeDPT)], has been determined by X-ray diffraction, and refined to a final R factor of 0.043 over 1771 reflections with $I > 3\sigma_{(I)}$. The compound crystallized from ethanol is monoclinic, space group $P2_1/a$, with the following cell constants: a = *21.249(4),* b = *13.669(3),* c = *6.816(2) Å, β = 93.01(2)(°), Z = 4.*

The structure is formed by discrete molecules in which the iron(II) ion shows a distorted trigonal bipyramid coordination. Bond lengths and some angles around the iron atom are Fe–O(1) = 1.954(3), Fe–O(2) = 1.951(3), Fe–N(1) = 2.096(4), Fe–N(2) = 2.090(4), Fe–N(3) = 2.190(4) Å, O(1)–Fe–O(2) = 136.9(2), O(1)–Fe–N(3) = 111.3(2), O(2)–Fe–N(3) = 111.8(2), N(1)–Fe–N(2) = 177.2(2)(°).

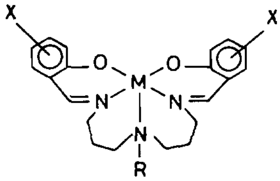
The molecule shows the presence of a non-crystallographic twofold symmetry axis colinear with the Fe–N(3) bond direction.

Introduction

It is well known that the study of the structures of the dioxygen adduct of iron and cobalt complexes, as well as the study of the conformational changes accompanying the coordination of dioxygen to metal complexes, is of great interest in understanding the mechanism of dioxygenation of the heme centers in hemoglobin and myoglobin. In particular for hemoglobin the mechanism of the cooperative oxygenation seems to involve small changes in the iron stereochemistry [1]. For these reasons the preparation and characterization of iron(II) and cobalt(II) complexes with tetra- and penta-coordinating ligand has recently received much attention.

Unfortunately structural investigations on the dioxygen adducts are rather rare because of the difficulties of preparing single crystals suitable for X-ray diffraction experiments.

We have recently obtained single crystals of the adduct $[Co(SALMeDPT)]_2 \cdot O_2 \cdot 2C_6H_6$ [2] and of the three forms of the precursor [Co(SALMeDPT)], one from acetone and two from benzene [3,4].



[M(X-SALRDPT)]

The X-ray analyses of the four species have shown the importance of the metal stereochemistry, as well as the importance of the crystal packing, in regard to the oxygenation process in the solid state. The syntheses, characterizations and reactivities towards dioxygen of iron(II) complexes of the type [Fe(X-SALRDPT)] have been recently reported [5].

As part of an extensive investigation on the structures of metal complexes which react with dioxygen and in particular metal complexes of the type [M(X-SALRDPT)] we have prepared [Fe(SALMeDPT)] by a different procedure and obtained single crystals from ethanol solution.

We report here the results of a single crystal X-ray analysis of this complex.

Experimental

Preparation of $Fe(CH_3COO)_2 \cdot 4H_2O$

An aqueous solution containing 6.60 g of glacial acetic acid (0.11 mol) in 50 ml of water was deaerated by bubbling ultrapure argon for half an hour. 2.79 g (0.05 mol) of reagent grade iron wire were added to the acidic solution and the mixture was stirred at 60–70 °C till complete dissolution of the metal. The green solution was dried and the excess of acetic acid removed under vacuum by a stream of argon at 60 °C. Analytical data of the iron content are in agreement with four molecules of water of crystallization. The salt was used without any further purification.

Preparation of [Fe(SALMeDPT)]

The complex was obtained from iron acetate by a procedure similar to that reported in Ref. 6 to obtain [Co(SALMeDPT)] and recrystallized from benzene.

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TABLE I. Crystal Data and Data Collection.

Molecular formula	$C_{21}H_{25}N_3O_2Fe$
Formula weight	485.4
Crystal symmetry	monoclinic
Space group	$P2_1/a$
a, b, c (Å)	21.249(4), 13.669(3); 6.816(2)
β (°)	93.01(2)
V (Å^3)	1977.0
Z	4
D_c (g/ml)	1.63
D_o (g/ml)	1.64
Crystal dimensions (mm)	0.2 × 0.2 × 0.1
$\mu_{(Mo K\alpha)}$ (cm^{-1})	7.65
Monochromatisation	Graphite monochromator
Scan type	$\theta-2\theta$ symmetric
Scan width (°)	1.40
Scan speed (°/sec)	0.06
Background time (sec)	5
θ max (°)	23
Number of unique intensities ($I > 3\sigma_I$[a])	1771
Number of parameters refined	314
Final R, Rw[b]	0.043, 0.049

[a] The standard deviation on intensity was calculated by: $\sigma_I = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{1/2}$ where P is the total integrated count obtained in time T_p, B_1 and B_2 are the background counts each collected in time T_b; $I = P - 0.5\,(T_p/P_b)(B_1 + B_2)$, and 0.02I is a correction for unrealistically small standard deviations in strong reflections. [b] $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$.

Single crystals suitable for X-ray analysis were prepared from a solution of the complex in ethanol evaporating the solvent by a slow stream of argon.

Structure Solution and Refinement

Crystal data and data collection procedure are reported in Table I. The intensities of three standard reflections were periodically monitored for stability control during data collection. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by the heavy atom technique, with the use of Patterson and electron density syntheses which gave all the non-hydrogen atom positions. Three cycles of least-squares refinement with isotropic temperature factors followed by two cycles with anisotropic temperature factors for all the atoms reduced the R factor to 0.080. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = a/(\sigma^2(F) + bF^2)$ where a and b were adjustable parameters. A difference Fourier synthesis calculated at this point clearly showed three new peaks around the N(3) atom. This fact was interpreted in terms of a two-fold orientational disorder around the Fe–N(3) axis. A similar behaviour was observed for other complex molecules containing the SALMeDPT ligand [2–4, 7]. On the basis of this hypothesis two sets of positions for the atoms C(17), C(20) and C(21) were refined, together with their occupancy factors compelled to reach the overall value of 1.00. All the thermal factors of these atoms were refined isotropically forcing the parameters of two corresponding atoms to assume the same value. A further Fourier difference synthesis computed at this stage was able to reveal clearly the positions of all the hydrogen atoms except those linked to the carbon atoms of the second set of the aminic chains. These atoms were introduced in the final refinement with a temperature factor U of 0.06 Å^2. The site occupation factor of the H(161) and H(191) atoms was tied with the occupancies of the C(17), C(20) and C(21) atoms.

Three additional least-squares cycles gave the final disagreement indices R and Rw of 4.3% and 4.9%. The weighting parameters were $a = 0.3970$, $b = 0.0058$. The occupancies for the atoms C(17), C(20) and C(21) were 0.60 and 0.40 for the two sets respectively. The positions of the atoms, as well as their thermal factors, are reported in Table II. All the calculations were performed with the Shelx-76 program [8] which uses the coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections both taken from Int. Tables [9]. The molecular plot was produced by ORTEP [10]. Observed and calculated structure factors are available as supplementary material.

Description of the Structure

The structure of [Fe(SALMeDPT)] consists of discrete molecules in which the metal center has a distorted trigonal bipyramidal coordination polyhedron

TABLE II. Final Atomic Coordinates ($\times 10^4$) and Thermal Parameters[a] ($Å^2 \times 10^4$) with Estimated Standard Deviations.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	2948(0)	76(0)	557(1)	487(4)	467(4)	401(4)	−20(3)	27(3)	−20(3)
O(1)	2438(2)	362(3)	2791(5)	553(22)	763(24)	432(19)	28(18)	−2(16)	−136(18)
O(2)	3246(2)	786(3)	−1697(5)	766(26)	710(25)	490(20)	−181(21)	−24(17)	113(18)
N(1)	2113(2)	−377(3)	−948(6)	600(29)	561(24)	422(25)	−61(20)	−29(21)	−69(19)
N(2)	3796(2)	456(3)	2055(6)	523(26)	648(27)	482(25)	29(23)	17(20)	−34(22)
N(3)	3258(2)	−1453(3)	584(6)	736(30)	498(24)	444(24)	48(22)	76(21)	12(20)
C(1)	1390(2)	291(4)	1322(8)	501(30)	448(29)	660(34)	−59(23)	27(25)	−5(25)
C(2)	1839(2)	527(3)	2891(7)	491(31)	440(26)	499(29)	−3(22)	67(23)	10(24)
C(3)	1600(3)	934(4)	4571(9)	672(41)	600(33)	639(39)	21(29)	152(30)	−73(30)
C(4)	979(3)	1111(4)	4747(11)	863(52)	611(38)	986(53)	26(32)	413(45)	−57(35)
C(5)	541(3)	897(5)	3202(13)	482(37)	756(42)	1409(71)	63(32)	277(44)	1(45)
C(6)	753(3)	504(5)	1560(11)	492(35)	728(40)	1023(51)	−70(30)	84(35)	−10(39)
C(7)	1551(3)	−207(4)	−455(8)	538(34)	590(34)	577(34)	−69(25)	−83(28)	−25(27)
C(8)	4118(2)	1673(4)	−256(8)	506(33)	553(32)	693(37)	4(24)	170(29)	−33(28)
C(9)	3672(3)	1477(4)	−1791(8)	598(34)	509(31)	613(34)	−33(26)	189(29)	41(27)
C(10)	3681(3)	2059(5)	−3485(10)	705(43)	787(43)	831(48)	56(36)	190(36)	261(38)
C(11)	4120(4)	2803(6)	−3586(14)	959(58)	844(52)	1240(79)	216(44)	571(60)	512(50)
C(12)	4555(4)	2993(6)	−2112(15)	603(46)	775(46)	1469(76)	7(37)	272(48)	214(53)
C(13)	4562(3)	2438(5)	−484(12)	681(44)	712(41)	1041(56)	−48(33)	188(38)	−63(44)
C(14)	4181(3)	1122(4)	1538(8)	443(30)	779(39)	616(36)	−3(28)	5(28)	−183(32)
C(15)	2213(3)	−984(5)	−2662(9)	813(44)	809(43)	461(35)	−105(35)	56(31)	−154(31)
C(16)	2442(4)	−1978(5)	−2067(12)	1167(68)	677(47)	800(51)	−75(40)	−43(46)	−282(39)
C(17)	2709(5)	−2111(9)	17(18)	763(24)					
C(17)′	3191(8)	−1899(12)	−1328(25)	763(24)					
C(18)	3953(3)	−104(5)	3864(8)	605(36)	982(49)	486(34)	137(35)	−54(27)	2(32)
C(19)	4086(4)	−1171(6)	3345(11)	1017(61)	1050(57)	653(46)	470(47)	−45(39)	206(42)
C(20)	3520(6)	−1760(8)	2496(16)	725(23)					
C(20)′	3928(8)	−1550(11)	1272(24)	725(23)					
C(21)	3738(6)	−1610(9)	−986(18)	739(24)					
C(21)′	2885(8)	−2008(13)	2067(27)	739(24)					

Atom[b,c]	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(3)	1891(25)	1036(39)	5560(79)	H(10)	3336(26)	1969(40)	−4230(79)
H(4)	841(22)	1434(36)	6143(72)	H(11)	4106(28)	3016(45)	−4511(84)
H(5)	107(26)	1068(36)	3194(73)	H(12)	4943(24)	3448(39)	−2082(70)
H(6)	467(24)	320(40)	430(73)	H(13)	4818(23)	2454(40)	656(85)
H(7)	1188(25)	−367(36)	−1482(75)	H(14)	4636(25)	1214(35)	2352(71)
H(151)	2487(25)	−700(38)	−3440(78)	H(181)	4309(25)	186(35)	4679(74)
H(152)	1826(25)	−974(37)	−3433(81)	H(182)	3619(27)	−82(36)	4591(81)
H(161)	2639(25)	−2261(40)	−3002(81)	H(191)	4409(26)	−1170(41)	2721(85)
H(162)	2167(26)	−2320(42)	−1803(90)	H(192)	4186(24)	−1458(38)	4435(78)
H(171)	2869(38)	−2566(62)	570(125)	H(201)	3169(43)	−1688(61)	3141(126)
H(172)	2477(39)	−1920(59)	1289(126)	H(202)	3579(35)	−2648(58)	2605(114)
H(211)	3583(36)	−1401(60)	−2296(131)				
H(212)	3845(38)	−2278(66)	−947(118)				
H(213)	4083(41)	−1195(63)	−540(122)				

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(\sum_{i}{}_1^3\sum_{j}{}_1^3 h_i h_j a_i^* a_j^* U_{ij})]$. [b] Hydrogen atoms are labelled according to the carbon atom to which they are attached. [c] The overall U thermal factor for all the hydrogen atoms was fixed to a value of 0.06 ($Å^2$).

(Fig. 1). The iron atom lies in the equatorial plane defined by the donors O(1), O(2) and O(3) (deviation of 0.007 Å) while the N(1) and N(2) nitrogen atoms are in the axial positions of the bipyramid. The most remarkable deviation from regular trigonal bipyramidal coordination geometry is due to the values of the equatorial bond angles O(1)–Fe–O(2), O(1)–Fe–N(3) and O(2)–Fe–N(3) which amount to 136.9(2)°, 111.3(2)° and 111.8(2)° respectively. In Table III are listed the bond lengths and angles in the

TABLE III. Bond Distances (Å) and Angles (°) with Estimated Standard Deviations.

Fe–O(1)	1.954(3)	Fe–O(2)	1.951(3)
Fe–N(1)	2.096(4)	Fe–N(2)	2.090(4)
Fe–N(3)	2.190(4)		
O(1)–C(2)	1.299(6)	O(2)–C(9)	1.312(6)
N(1)–C(7)	1.277(7)	N(2)–C(14)	1.285(7)
N(1)–C(15)	1.457(7)	N(2)–C(18)	1.475(7)
N(3)–C(17)	1.507(12)	N(3)–C(17)′	1.439(17)
N(3)–C(20)	1.452(11)	N(3)–C(20)′	1.482(16)
N(3)–C(21)	1.533(12)	N(3)–C(21)′	1.519(17)
O(1)–Fe–O(2)	136.9(2)	O(2)–Fe–N(2)	87.3(2)
N(1)–Fe–N(2)	177.2(2)	N(3)–Fe–O(1)	111.3(2)
O(1)–Fe–N(1)	87.2(2)	N(3)–Fe–O(2)	111.8(2)
O(1)–Fe–N(2)	93.9(2)	N(3)–Fe–N(1)	88.2(2)
O(2)–Fe–N(1)	93.6(2)	N(3)–Fe–N(2)	89.0(2)
Fe–O(1)–C(2)	131.3(3)	Fe–O(2)–C(9)	130.6(3)
Fe–N(1)–C(7)	126.6(4)	Fe–N(2)–C(14)	126.0(4)
Fe–N(1)–C(15)	113.9(4)	Fe–N(2)–C(18)	115.5(4)
C(7)–N(1)–C(15)	119.5(5)	C(14)–N(2)–C(18)	118.5(5)
Fe–N(3)–C(17)	109.9(5)	Fe–N(3)–C(17)′	112.4(7)
Fe–N(3)–C(20)	112.6(5)	Fe–N(3)–C(20)′	111.8(6)
Fe–N(3)–C(21)	109.8(5)	Fe–N(3)–C(21)′	108.4(7)
C(1)–C(2)	1.431(7)	C(8)–C(9)	1.400(8)
C(1)–C(6)	1.403(8)	C(8)–C(13)	1.422(8)
C(1)–C(7)	1.446(8)	C(8)–C(14)	1.437(8)
C(2)–C(3)	1.393(7)	C(9)–C(10)	1.403(8)
C(3)–C(4)	1.352(8)	C(10)–C(11)	1.384(11)
C(4)–C(5)	1.400(10)	C(11)–C(12)	1.354(12)
C(5)–C(6)	1.339(9)	C(12)–C(13)	1.343(10)
C(15)–C(16)	1.492(10)	C(18)–C(19)	1.532(10)
C(16)–C(17)	1.513(14)	C(19)–C(20)	1.535(13)
C(16)–C(17)′	1.647(18)	C(19)–C(20)′	1.525(18)
C(17)–N(3)–C(20)	108.3(7)	C(17)′–N(3)–C(20)′	107.2(10)
C(17)–N(3)–C(21)	105.8(7)	C(17)′–N(3)–C(21)′	111.2(10)
C(20)–N(3)–C(21)	110.3(7)	C(20)′–N(3)–C(21)′	105.7(10)
C(2)–C(1)–C(6)	118.4(5)	C(9)–C(8)–C(13)	119.1(6)
C(2)–C(1)–C(7)	123.7(5)	C(9)–C(8)–C(14)	124.4(5)
C(6)–C(1)–C(7)	117.9(5)	C(13)–C(8)–C(14)	116.5(6)
O(1)–C(2)–C(1)	122.5(4)	O(2)–C(9)–C(8)	122.9(5)
O(1)–C(2)–C(3)	120.8(5)	O(2)–C(9)–C(10)	119.2(5)
C(1)–C(2)–C(3)	116.6(5)	C(8)–C(9)–C(10)	118.0(5)
C(2)–C(3)–C(4)	122.9(6)	C(9)–C(10)–C(11)	119.7(7)
C(3)–C(4)–C(5)	120.6(6)	C(10)–C(11)–C(12)	122.6(7)
C(4)–C(5)–C(6)	118.3(6)	C(11)–C(12)–C(13)	118.9(7)
C(1)–C(6)–C(5)	123.2(6)	C(8)–C(13)–C(12)	121.7(7)
N(1)–C(7)–C(1)	124.8(5)	N(2)–C(14)–C(8)	124.9(5)
N(1)–C(15)–C(16)	111.1(5)	N(2)–C(18)–C(19)	109.7(5)
C(15)–C(16)–C(17)	117.8(7)	C(18)–C(19)–C(20)	115.8(7)
C(16)–C(17)–N(3)	114.5(8)	C(19)–C(20)–N(3)	116.4(8)
C(16)–C(17)′–N(3)	110.6(11)	C(19)–C(20)′–N(3)	115.1(11)
C(15)–C(16)–C(17)′	108.7(8)	C(18)–C(19)–C(20)′	120.2(8)

molecule with estimated standard deviations for all the non-hydrogen atoms.

It is interesting to note that the value of the O(1)–Fe–O(2) angle is smaller than the corresponding one in the [Ni(SALMeDPT)] complex (140.6(3)°) [7] but greater than the O(1)–Co–O(2) angles found in the structures of the [Co(SALMeDPT)] molecule of the α, β [3] and γ [4] forms as well as of the non-

TABLE IV. Equations of some Least-squares Planes with Deviations of the Atoms (Å) and Angles (deg) between the Planes.[a]

Plane	Atoms	Deviations	P	Q	R	S
1	O(1)	0.009	2.9133	12.4118	−2.7430	0.3850
	C(2)	0.012				
	C(3)	−0.013				
	C(4)	−0.023				
	C(5)	0.008				
	C(6)	0.032				
	C(1)	0.018				
	C(7)	−0.065				
	N(1)	0.023				
	Fe[b]	0.415				
2	O(2)	0.005	13.8123	−8.8407	−2.9460	4.2830
	C(9)	0.011				
	C(10)	0.008				
	C(11)	−0.014				
	C(12)	−0.015				
	C(13)	0.005				
	C(8)	0.001				
	C(14)	0.047				
	N(2)	−0.048				
	Fe[b]	0.442				
3	O(1)	0	17.0019	3.5513	3.3964	5.2216
	O(2)	0				
	N(3)	0				
	Fe[b]	0.007				
	1−2	109.9				
	1−3	97.6				
	2−3	97.8				

[a] The equations are of the form Px + Qy + Rz − S = O, with x, y, z fractional coordinates. [b] Not defining the plane.

TABLE V. Intermolecular Contact Distances Shorter than 3.600 Å.

Atom 1	Atom 2	Dist Å
x, y, z	x, y, z + 1	
C(3)	C(15)	3.446
C(18)	C(10)	3.528
	$\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}+1$	
C(4)	C(20)	3.595
	$\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$	
C(6)	C(12)	3.519
	$\bar{x}+1, \bar{y}, \bar{z}$	
C(13)	C(20)′	3.499

dioxygenated molecule of the [Co(SALMeDPT)]$_2$·O$_2$·2C$_6$H$_6$ adduct [2], which are 127.9(3)°, 126.9(3)°, 129.8(4)° and 120.4(7)° respectively.

The Fe–N separations are about 0.10 Å greater than the Ni–N separations in [Ni(SALMeDPT)] and

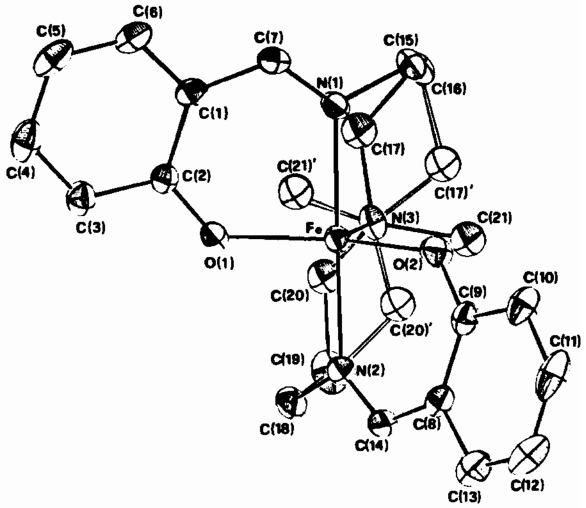

Fig. 1. ORTEP drawing of the molecule [Fe(SALMeDPT)] with the atom labelling. The empty sticks indicate the C–C and C–N bonds in the less probable set of peaks around N(3). The occupancies of the sets C(17), C(20), C(21) and C(17)′, C(20)′, C(21)′ are 0.60 and 0.40 respectively. Ellipsoids enclose 30% probability.

about 0.04 Å greater than the Co–N separations in [Co(SALMeDPT)]α, but they are in agreement with values from similar structures of high-spin iron(II) ions [11]. No differences exist between the Fe–O distances of this structure and the Ni–O and Co–O separations in the corresponding molecules.

Bond lengths and angles in the ligand molecules have normal values except for the angles at the carbon atoms of the trimethylene chains which are larger than those of the regular tetrahedron.

An interesting feature of this structure is the pattern of thermal motion. It appears from the drawing of Fig. 1 and from inspection of the thermal parameters (Table II) that the molecule is oscillating about an axis colinear with the Fe–N(3) bond direction.

The Fe–N(3) axis appears to be a non-crystallographic two-fold symmetry axis because of the existence of two sets of peaks around the position of the N(3) atom. This fact can be due to an orientational disorder of the molecules about the pseudo symmetry axis. This kind of pseudo-symmetry is noted also in the [Ni(SALMeDPT)] [7], [Co(SALMeDPT)]α, [Co(SALMeDPT)]β [3], [Co(SALMeDPT)]γ [4] complexes but it was not observed in the deoxygenated moiety in the adduct $[Co(SALMeDPT)]_2 \cdot O_2 \cdot 2C_6H_6$ [2]. Moreover, while the occupancies of the two sets of peaks around the N(3) atoms in the [Ni(SALMeDPT)], [Co(SALMeDPT)] α and β molecules have the value of 0.50, in the cases of the [Fe(SALMeDPT)] molecule and the [Co(SALMeDPT)] oxygenated molecule the site occupation factors are 0.60/0.40 and 0.65/0.35 respectively.

The equations of some significant least-squares planes are reported in Table IV. The iron atom is symmetrically displaced from the two salicylaldimine planes with separations of 0.415 and 0.442 respectively. It must be noted that the value of the dihedral angle between the salicylaldimine planes in this structure (109.9°) is slightly higher than the value of the corresponding angle in the [Co(SALMeDPT)]α complex (108.3°), in spite of the difference of 10° between the values of the O(1)–M–O(2) angles. This can be explained by the short intramolecular contacts between some carbon atoms of the trimethylene chains and of the salicylaldimine moieties: C(16)...... C(7) = 3.297 Å; C(17)...... C(7) = 3.585 Å; C(19)...... C(14) = 3.377 Å. As a consequence the C(7) and C(14) carbon atoms show the largest deviations from their planes.

An examination of the intermolecular contact separations does not show unusually short values or any kind of chemically important interactions. Selected intermolecular distances are listed in Table V.

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