Inorganica Chimica Acta, *175* (1990) 121-126

The ligand field stabilization effect on the metal–ligand bond distances in octahedral metal complexes with edta-type ligands. Redetermination of the molecular structure of (ethylenediaminetriacetatoacetic acid)-(aqua)iron(III), [Fe(Hedta)(H_2O)]

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(Received February 1, 1990; revised April 5, 1990)

Abstract

The molecular structure of the title complex [Fe(Hedta)(H_2O)] (Hedta = mono-protonated ethylenediamine-*N,N,N',N'*-tetraacetate) has been redetermined by single crystal X-ray diffraction methods. The crystal data are as follows: *monoclinic*, space *group* $P2_1/c$, $a=8.031(2)$, $b=8.897(2)$, $c=17.627(4)$ Å, $\beta=99.55(2)°$, $Z=4$ and $R=0.041$. The complex has an octahedral structure in which the protonated edta serves as a pentadentate ligand and a water molecule completes the six coordination. the M–L bond distances and L–M–L' bond angles redetermined are both comparable to those reported earlier, but the equatorial M–O bonds *trans* to the M–N bonds are shorter on average than the axial M–O bonds, at variance with the results of the earlier structure analysis in which the *R* value converged to 0.12. Detailed comparison of the M–L bond distances among several octahedral metal complexes with edta-type ligands including Hedta, demonstrates that the equatorial M–O bonds are longer on average than the axial ones for the Cr(III), Co(III) and Rh(III) complexes to which the ligand field stabilization (LFS) contributes greatly, while the reverse holds not only for the Fe(III) complexes but also for $[Al(edta)]^-$, $[Zn(edta)]^{2-}$, [Ga(Hedta)(H_2O)] and [Ge(Hedta)(OH)] to which there is no appreciable LFS contribution. The variation of the M–L bond distances with the M ion in these complexes has been discussed in relation to the LFS of the M ion.

Introduction

In our series of structural studies on transition metal complexes with edta-type ligands, it has been found that the equatorial M–O5 and M–O6 bonds *trans* to the M–N bonds are longer on average than the axial M–O7 and M–O8 bonds (Fig. 1) in octahedral Cr(III), Co(III) and Rh(III) complexes with edta, eddda (ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) and 1,3-pdta (1,3-propanediamine-*N,N,N',N'*-tetraacetate), while the reverse holds in the corresponding Fe(III) complexes [1, 2].

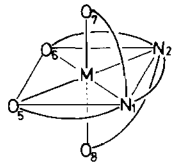

Fig. 1. Schematic structure of $[M(edta)]^{n-}$ complex.

We found quite recently that the Ge(IV)–edta complex, [Ge(Hedta)(OH)] (Hedta = mono-protonated edta), also has the equatorial M–O bonds shorter than the axial M–O bonds like the Fe(III) complexes [3]. Since the Ge(IV) complex bears a structural resemblance to the [M(Hedta)(H_2O)] type complexes isolated for some M(III) ions from acid solutions, the 'acid' Fe(III)–edta complex, [Fe(Hedta)(H_2O)] is expected to have shorter equatorial M–O bonds like other Fe(III) complexes. However, the structure analysis performed earlier on the acid Fe(III) complex, though comparatively poor in accuracy, suggests that the equatorial M–O bonds are longer on average by 0.05 Å than the axial ones [4], contrary to our expectation. Therefore, we undertook in the present study a redetermination of the molecular structure of the acid Fe(III) complex in a hope that our expectation would be fulfilled.

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0020-1693/90/$3.50

Experimental

Preparation of complex

Good-shaped yellow crystals of [Fe(Hedta)(H_2O)] were obtained by slow evaporation of an acidified aqueous solution of the complex prepared according to the procedures described in the literature [4, 5].

X-ray measurements

Determination of cell constants and collection of intensity data of reflection were carried out as before [2] on a Syntex R-3 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) by an ω scan mode up to $2\theta = 55°$. No correction was made for the absorption effect (μ(Mo Kα) = 12.24 cm^{-1}). Out of 3352 reflections measured, 2557 reflections with $|F_o| > 3\sigma(F_o)$ were included in the structure analysis.

Crystal data

Monoclinic, space group $P2_1/c$, $a = 8.301(2)$, $b = 8.897(2)$, $c = 17.627(4)$ Å, $\beta = 99.55(2)°$, $V = 1283.8(5)$ Å^3, $\rho_{calc} = 1.878$ g/cm^3 and $Z = 4$. Based on these data, it is confirmed that all of the three axes are somewhat shorter and the angle β is slightly wider than those reported earlier by Kennard [4], and that the isostructural [Fe(Hedta)(H_2O)], [Ga(Hedta)(H_2O)] [4], [Cr(Hedta)(H_2O)] [6] and [Rh(Hedta)(H_2O)] [7] are all isomorphous, whereas [Co(Hedta)(H_2O)] is not [8], probably because of its much smaller size.

Determination and refinement of a structure

The structure was solved by the same procedures as applied previously [1–3]. The quantity minimized in the refinement was $\Sigma w(|F_o| - k|F_c|)^2$ and the weighting scheme used was $w = (\sigma cs^2)^{-1}$, where σcs is the standard deviation obtained from the counting statistics. The final refinement including hydrogen atoms with isotropic temperature factors converged the R and R_w values to 0.041 and 0.043, respectively, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

All the computations were carried out on a HITAC M-680H computer using the programs UNICS-III [9] and ORTEP [10]. The final positional and thermal parameters are given in Table 1, according to the labeling schemes adopted in Fig. 2.

Results and discussion

Description of molecular structure

The molecular structure (ORTEP) of the acid Fe(III) complex, [Fe(Hedta)(H_2O)], is depicted in Fig. 2, and bond distances and angles within the

TABLE 1. Positional and thermal parameters for [Fe(Hedta)(H_2O)][a]

Atom	x	y	z	B_{eq} (Å^2)[b]
Fe	0.30869(6)	0.33685(5)	0.85748(2)	1.4
N1	0.1331(3)	0.2335(3)	0.92576(14)	1.4
N2	0.3265(3)	0.1066(3)	0.82226(14)	1.5
O1	−0.2481(3)	0.4082(3)	0.95689(14)	2.4
O2	0.7136(3)	0.2149(3)	0.77985(14)	3.0
O3	0.4599(3)	0.2775(3)	1.08788(12)	2.4
O4	0.0155(3)	0.2158(3)	0.66387(14)	3.2
O5	−0.1766(3)	0.1688(3)	0.97563(14)	2.7
O6	0.5052(3)	0.3433(3)	0.81208(12)	2.1
O7	0.4430(3)	0.3241(3)	0.96292(12)	1.8
O8	0.1345(3)	0.3399(3)	0.76807(12)	2.0
OW	0.2794(3)	0.5583(3)	0.86916(13)	2.5
C1	0.0912(4)	0.0837(4)	0.88889(18)	1.7
C2	0.2463(4)	0.0082(4)	0.87314(19)	1.9
C3	−0.1493(4)	0.2921(4)	0.95422(17)	1.8
C4	−0.0057(4)	0.3382(4)	0.91663(17)	1.7
C5	0.5841(4)	0.2184(4)	0.80352(17)	2.0
C6	0.5041(4)	0.0782(4)	0.82813(19)	2.0
C7	0.3838(4)	0.2778(4)	1.02219(17)	1.5
C8	0.2115(4)	0.2189(4)	1.00737(17)	1.8
C9	0.1191(4)	0.2247(4)	0.72168(18)	1.9
C10	0.2418(4)	0.1000(4)	0.74138(19)	2.2

[a]e.s.d.s given in parentheses. [b]$B_{eq} = 8/3\pi^2(U_{11} + U_{22} + U_{33})$.

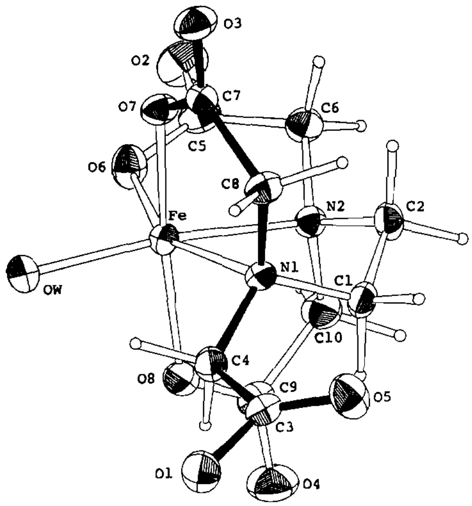

Fig. 2. Molecular structure (ORTEP) of [Fe(Hedta)(H_2O)].

complex are listed in Tables 2 and 3, respectively, both of which are roughly comparable to those reported earlier by Kennard in 1967 [4].

Figure 2 indicates that Hedta is acting as a pentadentate ligand with one protonated acetate group freed from coordination and with a water molecule occupying the sixth coordination site, forming thereby a six-coordinate complex with the Fe(III) ion, and that the protonated acetate group is the one which should otherwise form a G chelate ring. Comparison of the C3–O1 and C3–O5 bond distances ensures that the proton is attached to the O1 atom *trans* to the N1 atom. All of these structural features are in complete agreement with those reported earlier, and they are common to all acid complexes of the type [M(Hedta)(H_2O)] [4, 6–8] and to [Ge(Hedta)(OH)] [3] in which the sixth coordination site is occupied by an OH^- ion.

Characteristics of bite angles L–M–L′

The molecular structure shown in Fig. 2 also indicates that the Fe(III) complex is subjected to considerable distortion from a regular octahedral structure, which is seen more clearly from the bite angles L–M–L′ given in Table 3; the bite angles associated with the chelate rings, i.e. the N1–Fe–N2, N1–Fe–O7, N2–Fe–O6 and N2–Fe–O8 angles are fairly narrower, while the N1–Fe–OW, N2–Fe–O7, O6–Fe–O8 and O6–Fe–OW angles not associated with them are wider, than an ideal angle of 90° for a regular octahedron. Similar angular deviations, though smaller in magnitude, are also found in other acid complexes including [Ge(Hedta)(OH)] [3, 4, 6–8].

The degree of angular deviation is evaluated quantitatively by the parameters $\Sigma(\alpha_i - 90°)^2$ [2], where α_i stands for each L–M–L′ angle in degrees (twelve angles in all). The value is estimated to be 950 for the acid Fe(III)–edta complex, which is much greater than those for other acid complexes; 103, 264, 351, 447 and 462 for the Co(III) [8], Rh(III) [7], Ge(IV) [3], Cr(III) [6] and Ga(III) [4] complexes, respectively. In addition, the parent complex, $[Fe(edta)]^-$ is also distorted greatly; its distortion parameter amounts to 1703 [11] and is comparable to 1823 [12] or 1737 [13] estimated for $[Mn(III)(edta)]^-$ which is distorted inevitably by the Jahn–Teller effect*. The greatly distorted structures of the above two Fe(III) complexes are attributed to a comparatively large size of the Fe(III) ion for a tervalent ion and to no appreciable angular dependence of the ligand field stabilization for the Fe(III) ion with a high-spin $3d^5$ electronic configuration [1, 2].

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*Since the $[Cu(edta)]^{2-}$ complex deforms by the Jahn–Teller effect so as to relieve the strain imposed on the G chelate rings, its angular distortion is less than is supposed, its distortion parameter being 785 only [14]. In contrast, the $[Mn(edta)]^-$ complex deforms so as to reinforce the strain so that its distortion parameter amounts to a much higher value of 1823 or 1737 [12, 13].

TABLE 2. Intramolecular bond distances (Å) in [Fe(Hedta)(H_2O)]^a

Bond		Bond		Bond	
Fe–N1	2.237(3)	N2–C2	1.488(4)	O6–C5	1.312(4)
Fe–N2	2.152(3)	N2–C6	1.482(4)	O7–C7	1.293(4)
Fe–O6	1.933(2)	N2–C10	1.482(4)	O8–C9	1.304(4)
Fe–O7	2.006(2)	O1–C3	1.324(4)	C1–C2	1.518(5)
Fe–O8	1.954(2)	O2–C5	1.217(4)	C3–C4	1.514(5)
Fe–OW	2.000(2)	O3–C7	1.223(4)	C5–C6	1.510(5)
N1–C1	1.498(4)	O4–C9	1.222(4)	C7–C8	1.506(5)
N1–C4	1.469(4)	O5–C3	1.194(4)	C9–C10	1.507(5)
N1–C8	1.483(4)				

^{a}e.s.d.s given in parentheses.

TABLE 3. Intramolecular bond angles (°) in [Fe(Hedta)(H_2O)][a]

Angle		Angle		Angle	
N1–Fe–N2	81.13(10)	Fe–N1–C4	104.43(19)	O1–C3–O5	123.7(3)
N1–Fe–O6	154.83(10)	Fe–N1–C8	109.74(19)	O1–C3–C4	110.0(3)
N1–Fe–O7	77.87(9)	C1–N1–C4	113.3(3)	O5–C3–C4	126.3(3)
N1–Fe–O8	88.77(10)	C1–N1–C8	112.1(2)	N1–C4–C3	116.1(3)
N1–Fe–OW	104.40(10)	C4–N1–C8	111.8(3)	O2–C5–O6	123.2(3)
N2–Fe–O6	78.81(10)	Fe–N2–C2	109.10(19)	O2–C5–C6	122.2(3)
N2–Fe–O7	99.17(10)	Fe–N2–C6	104.91(19)	O6–C5–C6	114.5(3)
N2–Fe–O8	81.82(10)	Fe–N2–C10	105.7(2)	N2–C6–C5	108.6(3)
N2–Fe–OW	169.25(10)	C2–N2–C6	113.4(3)	O3–C7–O7	124.0(3)
O6–Fe–O7	90.44(10)	C2–N2–C10	111.6(3)	O3–C7–C8	119.3(3)
O6–Fe–O8	103.18(10)	C6–N2–C10	111.6(3)	O7–C7–C8	116.6(3)
O6–Fe–OW	97.96(10)	Fe–O6–C5	119.6(2)	N1–C8–C7	112.9(3)
O7–Fe–O8	166.23(10)	Fe–O7–C7	122.6(2)	O4–C9–O8	123.8(3)
O7–Fe–OW	91.06(10)	Fe–O8–C9	118.5(2)	O4–C9–C10	120.0(3)
O8–Fe–OW	89.03(10)	N1–C1–C2	109.3(3)	O8–C9–C10	116.2(3)
Fe–N1–C1	104.93(18)	N2–C2–C1	109.2(3)	N2–C10–C9	112.8(3)

[a] e.s.d.s given in parentheses.

Characteristics of bond distances M–L

It is notable in Table 2 that the Fe–N2 bond is shorter (by 0.085 Å) than the Fe–N1 bond, whereas the Fe–OW bond *trans* to the Fe–N2 bond is longer (by 0.067 Å) than the Fe–O6 bond in the [Fe(Hedta)(H_2O)] complex. Exactly the same tendency has been found in other acid complexes of the type [M(Hedta)(H_2O)] (M = Cr(III), Co(III), Ga(III) and Rh(III) [4, 6–8]), as seen in Table 4, where the M–L bond distances are compared among these acid complexes. The long M–OW bond may be due to the intermolecular hydrogen bonds, as pointed out for the Rh(III) complex by Lin *et al.* [7], and/or to the fact that the OW atom is electrically neutral, while the O6 atom carries a formal negative charge. However, if the M–L bond distances are compared between a parent complex [M(edta)]$^-$ and the corresponding [M(Hedta)(H_2O)], it is evident in Table 4 that the M–N1 bond is lengthened,but the M–O6 bond *trans* to that bond is shortened when each [M(edta)]$^-$ complex rearranges to the [M(Hedta)(H_2O)] complex upon protonation (M = Fe(III) [11], Cr(III) [15] and Co(III) [16]). Since these changes are observed for the Co(III) complex as well whose chemical composition (trihydrate), space group ($P2_12_12_1$) and crystal system (orthorhombic) are all different from those of other acid complexes, the shorter M–N2 and longer M–OW bonds observed in common for these acid complexes come from their intrinsic properties.

It is interesting to note that the M–N2 and M–O8 bonds, and M–OW(5) and M–O7 bonds are somewhat shortened, and lengthened respectively, upon protonation for both the Fe(III) and Cr(III) complexes, while the completely reverse changes are observed for the Co(III) complex, though small in magnitude. Consequently, the M–O7 bond is longer than the M–O8 bond in the acid Fe(III) and Cr(III) complexes

TABLE 4. Comparison of M–L bond distances (Å) in [M(Hedta)(H_2O)] and [M(edta)]$^-$ complexes

Complex	M–N1	M–N2	M–OW(5)	M–O6	M–O7	M–O8	Reference
[Fe(Hedta)(H_2O)]	2.237(3)	2.152(3)	2.000(2)[a]	1.933(2)	2.006(2)	1.954(2)	this work
[Cr(Hedta)(H_2O)]	2.141(2)	2.041(2)	2.002(2)[a]	1.932(2)	1.980(2)	1.935(2)	6
[Co(Hedta)(H_2O)]	1.986(6)	1.937(6)	1.927(5)[a]	1.913(6)	1.881(5)	1.896(5)	8
[Ga(Hedta)(H_2O)]	2.182(5)	2.097(6)	1.951(6)[a]	1.924(5)	1.996(4)	1.953(5)	4
[Rh(Hedta)(H_2O)]	2.082(3)	1.988(3)	2.096(2)[a]	2.027(3)	2.030(3)	2.001(3)	7
[Ge(Hedta)(OH)]	2.106(5)	2.081(5)	1.768(5)[b]	1.876(5)	1.892(5)	1.882(4)	3
[Fe(edta)]$^-$	2.181(4)	2.178(3)	1.973(3)[c]	1.967(3)	1.970(3)	1.987(3)	11
[Cr(edta)]$^-$	2.044	2.059	1.969[c]	1.999	1.952	1.965	15
[Co(edta)]$^-$	1.921(8)	1.929(8)	1.945(7)[c]	1.946(7)	1.897(7)	1.887(7)	16

[a] M–OH_2 bond. [b] M–OH bond. [c] M–O5 bond.

TABLE 5. Comparison of M–L bond distances (Å) corrected for the ionic radius of M

Complex	d^n	$r(M)^a$	$r(M–O)_{ax}-r(M)$	$r(M–O)_{eq}-r(M)$	$r(M–N)_{eq}-r(M)$	Reference
[Ge(Hedta)(OH)]	10	0.670	1.22	1.15	1.42	3
[Fe(Hedta)(H_2O)]	5	0.785	1.20	1.18	1.41	this work
[Ga(Hedta)(H_2O)]	10	0.760	1.21	1.18	1.36	4
[Cr(Hedta)(H_2O)]	3	0.755	1.20	1.21	1.34	6
[Co(Hedta)(H_2O)]	6	0.685	1.20	1.24	1.28	8
[Rh(Hedta)(H_2O)]	6	0.805	1.21	1.26	1.23	7
$[Al(edta)]^-$	0	0.675	1.22	1.18	1.38	19
$[Fe(edta)]^-$	5	0.785	1.19	1.18	1.39	11
$[Cr(edta)]^-$	3	0.755	1.20	1.23	1.30	15
$[Co(edta)]^-$	6	0.685	1.21	1.26	1.24	16
$[Mn(edta)]^-$	4	0.785	1.12	1.23	1.41	12
$[Zn(edta)]^{2-}$	10	0.880	1.24	1.17	1.27	14
$[Co(edta)]^{2-}$	7	0.885	1.22	1.18	1.27	20
$[Ni(edta)]^{2-}$	8	0.830	1.23	1.24	1.25	21
$[Cu(edta)]^{2-}$	9	0.870	1.38	1.12	1.17	14
$[Fe(1,3\text{-}pdta)]^-$	5	0.785	1.21	1.20	1.41	1
$[Cr(1,3\text{-}pdta)]^-$	3	0.755	1.19	1.21	1.31	22
$[Co(1,3\text{-}pdta)]^-$	6	0.685	1.18	1.22	1.28	23
$[Rh(1,3\text{-}pdta)]^-$	6	0.805	1.20	1.24	1.23	22
$[Fe(eddda)]^{-\,b}$	5	0.785	1.22	1.15	1.42	1
$[Cr(eddda)]^{-\,b}$	3	0.755	1.20	1.21	1.33	24
$[Co(eddda)]^{-\,b}$	6	0.685	1.20	1.23	1.27	2
$[Rh(eddda)]^{-\,b}$	6	0.805	1.20	1.24	1.22	25

[a] Taken from ref. 18. [b] *Trans*(O_5) isomer.

and in other acid complexes as well, except for the acid Co(III) complex in which the M–O7 bond is slightly shorter than the M–O8 bond. The exceptional behavior of the acid Co(III) complex comes at least in part from the fact that the complex is different in chemical composition, space group and crystal system from other acid complexes.

Variation of M–L bond distances with M

First of all, it is confirmed in Table 4 that the equatorial M–OW and M–O6 bonds are actually shorter on average, as we expected, than the axial M–O7 and M–O8 bonds in [Fe(Hedta)(H_2O)] as in other Fe(III) complexes with edta-type ligands [2] and in [Ga(Hedta)(H_2O)] [4] and [Ge(Hedta)(OH)] [3], the equatorial M–O bonds estimated earlier for [Fe(Hedta)(H_2O)] being too long [4].

In order to examine the variation of the M–L bond distances with the M ion, it is fruitful to compare the M–L bond distances corrected for the contribution of the ionic radius of the M ion. For this purpose, the crystal radii r(M) defined by Fumi and Tosi [17] and tabulated by Shannon [18] are employed. In Table 5 are given average values of the axial M–O, equatorial M–O and equatorial M–N bond distances from each of which the crystal radius of the respective M ion, r(M), is subtracted, i.e., $r(M–O)_{ax}-r(M)$, $r(M–O)_{eq}-r(M)$ and $r(M–N)_{eq}-r(M)$, for the [M(Hedta)(H_2O)] complexes including [Ge(Hedta)(OH)] [3, 4, 6–8].

It is noteworthy in Table 5 that the value of $r(M–O)_{ax}-r(M)$ remains almost constant (1.21 Å on average), while those of $r(M–O)_{eq}-r(M)$ and $r(M–N)_{eq}-r(M)$ change systematically with M; the former increases in the order Ge(IV) < Fe(III) ≈ Ga(III) < Cr(III) < Co(III) < Rh(III), and the latter increases in the completely reverse order. These observations lead us to propose that the affinity of the M ion for the O ligator increases in the order Rh(III) < Co(III) < Cr(III) < Ga(III) ≈ Fe(III) < Ge(IV), while that for the N ligator increases in the reverse order. Since the ligand field stabilization (LFS) increases in the order Ge(IV) ($3d^{10}$) ≈ Fe(III) (high-spin $3d^5$) ≈ Ga(III) ($3d^{10}$) < Cr(III) ($3d^3$) < Co(III) (low-spin $3d^6$) < Rh(III) (low-spin $4d^6$), it follows that the greater the LFS of the M ion, the stronger its affinity for the N ligator. In contrast, those M ions to which no appreciable LFS contributes, interact favorably with the O ligator, probably through an electrostatic force in the main. A typical example is provided by the Ge(IV) complex in which the central metal ion is tetravalent and the equatorial M–O bonds are thus by far short.

Exactly the same tendency as above is found in other metal complexes with edta and its related ligands, as seen in Table 5; the affinity of the M(III) ion for the O or N ligator varies in the same order as found in the Hedta complexes. In addition, Al(III) ($3d^0$) and Zn(II)($3d^{10}$) ions show a stronger affinity for the O ligator, as expected from their electronic configurations, and the Co(II) ion (high-spin $3d^7$) favors the O ligator slightly over the N ligator, while the Ni(II) ion ($3d^8$) seems to behave oppositely. Unusual bond distances found in $[Mn(edta)]^-$ and $[Cu(edta)]^{2-}$ are attributed to the Jahn–Teller effect expected for the high-spin d^4 and the d^9 configurations, respectively. In this way, the equatorial M–O and M–N bond distances vary in conformity with the electronic and electrostatic demands of the central metal ion M. In contrast, the axial M–O bond distances corrected for the crystal radius of M are almost indifferent to the nature of the M ion, probably because the mutual *trans* influence cancels out between the two axial O atoms *trans* to each other.

Supplementary material

Observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

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