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Low-Temperature Neutron and X-Ray Diffraction Studies on $Mn(cth)Cu(oxpn)(CF_3SO_3)_2$: (cth) = (±)-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane; (oxpn) = *N,N'*-Bis(3-aminopropyl)oxamide

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The present investigation shows the complementarity of neutron and X-ray diffraction studies. Neutron and X-ray diffraction experiments on a single crystal of Mn(cth)Cu(oxpn)$(CF_3SO_3)_2$ have been performed in order to study the nuclear structure and to form the basis for a spin distribution study of this heterodinuclear compound.

The nuclear structure at room temperature has been previously reported. We now report the crystal structure at low temperatures, 25 and 40 K for X-ray and neutron experiments, respectively. No phase transition has been found between room temperature and 25 K. The compound crystallizes in a monoclinic system, space group $P2_1/a$ with 100 atoms in the unit cell. The unconventional space group is used to be consistent with the room-temperature study. The lattice parameters at low temperature are $a = 17.525(3)$ Å, $b = 17.955(4)$ Å, $c = 12.804(2)$ Å, and $\beta = 104.97(2)°$ with $Z = 4$.

The structure consists of an oxamido-bridged $Mn^{II}Cu^{II}$ part and two uncoordinated triflate anions. The Mn^{II} ion is in an elongated octahedral surrounding, and the Cu^{II} ion in a square-planar surrounding. The intramolecular Mn···Cu separation is 5.450(1) Å, whereas the shortest intermolecular metal–metal Mn···Cu separation is equal to 7.840(1) Å.

In disagreement with the previous X-ray study at room temperature, we have found both anions to have disordered fluorine atoms around the carbon atoms C(20) and C(21). The C(3)–C(4)–C(5) hydrocarbonated chain is described in a disordered model with two different configurations.

For several years $Mn^{II}Cu^{II}$ bimetallic species have been studied. Up to now the efforts have concerned the controlled synthesis of such compounds and the understanding of the magnetic properties by means of polarised neutron diffraction experiments (pnd) in particular. Previously a pnd data collection on a single crystal of Mn(cth)Cu(oxpn)$(CF_3SO_3)_2$ had been performed in order to determine the spin distribution of this heterodinuclear compound.[1] One purpose of the present investigation is to provide nuclear structure factors for the analysis in the pnd study.

A neutron diffraction study at 40 K has been completed and 3301 reflections with an intensity greater than 2σ have been collected. However, this was not sufficient to refine all parameters. As a matter of fact, the number of atoms, namely 100 per unit cell, including 52 hydrogen atoms for which accurate data were needed, led us to believe that a combination of X-ray and neutron diffraction data was the best way to solve this problem. The X-ray study at low temperature (25 K) has allowed us to collect 7280 independent reflections which were necessary to solve the disorder problems.

Experimental

Synthesis and crystal growth. Mn(cth)$(CF_3SO_3)_2$ and Cu(oxpn) were succesfully synthesized by C. Mathoniere as previously described.[2,3] A large and well shaped brown

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single crystal was obtained by slow evaporation from saturated diethyl oxide solutions of $Mn(cth)(CF_3SO_3)_2$ and Cu(oxpn) mixed together. A single crystal, $6 \times 4 \times 2$ mm, was used for the polarised neutron diffraction experiment as well as for the present neutron diffraction experiment. A small piece of the same crystal, 0.617×10^{-2} mm^3, has been used for the X-ray experiment.

X-Ray data collection and structure refinement. X-Ray diffraction data were collected with the four-circle diffractometer at the Institute of Chemistry, Uppsala University. Unit-cell dimensions were obtained from least-squares refinement of the setting angles of 25 well centered high-angle reflexions using Mo $K_{\alpha 1}$ radiation. Crystallographic data and information concerning data collection and structure refinement are summarized in Tables 1 and 2. The six reference reflections monitored during the data collection showed no significant deterioration ($\pm 1\%$). Corrections were made for Lorentz, polarization and absorption effects. All calculations were performed using the Uppsala Crystallographic Computer Programs[4] and the TEXSAN system.[5] Isotropic extinction corrections were applied in the general case by refinement of type I and type II extinction coefficients.[6] They were found to be very small ($e_I = 0.103 \times 10^5$, $e_{II} = 0.199 \times 10^5$). The mean radius mosaic block size has been determined to be 0.014 mm. Scattering factors for the atoms were taken from Ref. 7.

The X-ray structure at 25 K was refined with a starting model from the structure at room temperature.[2] Both positional and anisotropic displacement parameters for heavy atoms were refined, whereas atomic positions and isotropic displacement parameters for the hydrogen atoms were calculated. Mathoniere *et al.*[2] reported that one of the two triflate anions appeared to be disordered. In our refinements, we found both triflate anions to be disordered, one more so than the other. Several attempts to model this disorder were unsucessful because the difference electron density map revealed several peaks in the immediate vinicity of the anions, especially of the most disordered anion. Models with three, five and six fluorines in the triflate anions have been tested but the results from these models are similar. In fact the best fit was obtained with five positions for the three fluorine atoms. Figure 2 shows the very elongated ellipsoids from a refinement with only three positions for the fluorine atoms. In order to describe the big C(3), C(4), C(5) thermal anisotropies, six carbon positions C(31), C(32), C(41), C(42), C(51), C(52) have been calculated on both sides of the equivalent refined C(3), C(4), C(5) positions. The atomic positions as well as the isotropic thermal parameters for these carbons have been fixed in the refinement, whereas the site occupations have been refined and found to be close to 0.5.

Table 1. Crystal data of $Mn(cth)Cu(oxpn)(CF_3SO_3)_2$.

Chemical formula	$C_{26}H_{52}F_{10}N_8O_8S_2CuMn$
a/Å	17.525(3)
b/Å	17.955(4), $\beta = 104.97(2)^\circ$
c/Å	12.804(2)
FW	897.308
Space group	$P2_1/a$
V/Å^3	3892.19
Z	4

Table 2. Details of the data collection and structure refinement.

		Neutron		
Diffraction technique	X-ray	Model A	Model B	Model C
Diffractometer	Huber four-circle		Huber four-circle	
λ /Å	0.71069 (MoKα)		1.215	
Monochromator	graphite		Cu (220) double system	
Crystal volume (mm^3)	0.617×10^{-2}		48	
T/K	25		40	
ρ(calc)/g cm^{-3}	1.54		1.54	
μ/cm^{-1}	9.005		2.17	
e_I	0.103×10^5		0.942×10^4	
e_{II}	0.199×10^5		0.179×10^5	
Max. value of sin θ/λ	0.597		0.529	
No. of standard reflexions and variation (%)	6 ± 1		3 ± 2	
No. of independent reflexions measured	7280		6537	
Reflexions used	5199		2864	
No. of parameters	483	433	415	445
Internal agreement factor	0.008	0.036	0.036	0.036
$R(F_o)$	0.057	0.083	0.094	0.077
$R_w(F_o)$	0.072	0.087	0.091	0.073
S	3.6	4.34	4.51	3.62

Agreement factors are refined as follows: $R = \Sigma||F_o| - ||/\Sigma|F_o|$; $R_w = [\Sigma w(||F_o| - |F_o||)^2/[w|F_o|^2]^{1/2}]$; $s = [\Sigma w(|F_o| - |F_o|)^2/(NO - NV)]^{1/2}$.

5199 reflexions greater than 4σ have been used to refine a total of 483 parameters. The convergence was reached with the R and R_w values listed in Table 2. No significant features could be found in the final difference Fourier map. Atomic coordinates for the heavy atoms are given in Table 3. A brief report of atomic distances are listed in Table 4. Some least-squares planes around Mn and Cu are given in Table 5.

Table 3. Internal *xyz* atomic coordinates obtained with the X-ray data collection refinement at 25 K.

Atom	*x*	*y*	*z*	B_{iso}/Å^2	Occupancy
Cu	0.36905(4)	0.17044(4)	0.07993(5)	0.82(3)	1
Mn	0.39299(5)	0.26529(5)	−0.31470(6)	0.80(3)	1
O(1)	0.3055(2)	0.2355(2)	−0.2294(3)	0.9(1)	1
O(2)	0.4645(2)	0.2355(2)	−0.1565(3)	1.2(2)	1
O(11)	0.8262(3)	0.6136(3)	0.2716(4)	3.8(2)	1
O(12)	0.8222(3)	0.4795(2)	0.2545(3)	1.8(2)	1
O(13)	0.9364(2)	0.5462(3)	0.2309(3)	2.2(2)	1
O(21)	0.4717(4)	0.3153(3)	0.2576(7)	8.9(4)	1
O(22)	0.3635(3)	0.2742(3)	0.3230(3)	3.4(2)	1
O(23)	0.4338(3)	0.3885(3)	0.3912(3)	4.2(2)	1
N(1)	0.2984(3)	0.1928(3)	−0.0600(4)	1.0(2)	1
N(2)	0.4514(3)	0.1884(3)	0.0075(3)	1.1(2)	1
N(3)	0.4446(3)	0.1364(3)	0.2189(4)	1.2(2)	1
N(4)	0.2818(3)	0.1657(3)	0.1551(4)	1.2(2)	1
N(5)	0.4918(3)	0.3105(3)	−0.3811(3)	1.0(2)	1
N(6)	0.4341(3)	0.1572(3)	−0.3748(3)	0.8(2)	1
N(7)	0.3536(3)	0.3861(3)	−0.3109(4)	1.0(2)	1
N(8)	0.2998(3)	0.2697(3)	−0.4738(3)	0.9(2)	1
C(1)	0.3353(3)	0.2149(3)	−0.1311(4)	0.9(2)	1
C(2)	0.4251(3)	0.2136(3)	−0.0904(4)	0.9(2)	1
C(31)	0.5374	0.1912	0.0513	1.5	0.49(2)
C(32)	0.5374	0.1736	0.0513	1.5	0.51(2)
C(41)	0.5658	0.1422	0.1539	1.5	0.46(1)
C(42)	0.5658	0.1652	0.1539	1.5	0.54(1)
C(51)	0.5296	0.1199	0.2311	1.5	0.47(1)
C(52)	0.5296	0.1421	0.2311	1.5	0.53(1)
C(6)	0.2116(4)	0.1910(4)	−0.0958(5)	2.3(3)	1
C(7)	0.1756(4)	0.1546(4)	−0.0149(5)	2.5(3)	1
C(8)	0.2000(3)	0.1880(4)	0.0950(5)	2.0(3)	1
C(9)	0.5419(3)	0.2450(3)	−0.3823(5)	1.4(2)	1
C(10)	0.4907(3)	0.1790(3)	−0.4380(5)	1.4(2)	1
C(11)	0.3729(3)	0.1004(3)	−0.4290(4)	1.0(2)	1
C(12)	0.3094(3)	0.1353(3)	−0.5231(4)	1.0(2)	1
C(13)	0.2548(3)	0.1984(3)	−0.5002(5)	1.2(2)	1
C(14)	0.2498(3)	0.3332(3)	−0.4617(5)	1.3(2)	1
C(15)	0.3013(3)	0.4006(3)	−0.4188(5)	1.4(2)	1
C(16)	0.4150(3)	0.4430(3)	−0.2680(5)	1.1(2)	1
C(17)	0.4791(3)	0.4428(3)	−0.3300(5)	1.4(2)	1
C(18)	0.5353(3)	0.3755(3)	−0.3219(5)	1.4(2)	1
C(20)	0.8070(4)	0.5552(5)	0.0806(7)	3.9(4)	1
C(21)	0.3438(7)	0.3855(5)	0.2009(8)	6.5(5)	1
C(111)	0.4103(3)	0.0357(3)	−0.4735(4)	1.2(2)	1
C(112)	0.3358(3)	0.0711(3)	−0.3418(5)	1.3(2)	1
C(131)	0.1830(4)	0.2060(3)	−0.5979(5)	1.8(2)	1
C(161)	0.4506(3)	0.4257(3)	−0.1486(5)	1.4(2)	1
C(162)	0.3799(4)	0.5209(3)	−0.2786(5)	2.0(3)	1
C(181)	0.6057(4)	0.3986(4)	−0.3658(5)	2.1(3)	1
S(1)	0.85342(9)	0.54881(8)	0.2270(1)	1.38(6)	1
S(2)	0.4110(1)	0.33568(9)	0.3042(1)	1.64(6)	1
F(11)	0.7313(7)	0.5349(4)	0.0519(9)	1.6(4)	1/2
F(12)	0.8296(8)	0.6323(7)	0.0635(9)	3.0(6)	1/2
F(13)	0.8300(3)	0.4997(3)	0.0282(3)	5.2(3)	1
F(14)	0.7266(6)	0.5733(6)	0.0759(9)	3.4(5)	1/2
F(15)	0.8226(8)	0.6064(6)	0.0230(8)	1.7(4)	1/2
F(21)	0.3373(4)	0.3341(4)	0.1057(5)	0.9(2)	1/2
F(22)	0.2851(7)	0.3513(6)	0.1411(8)	6.1(6)	1/2
F(23)	0.2856(3)	0.4103(4)	0.240(1)	17.8(6)	1
F(24)	0.3531(5)	0.4520(4)	0.1820(6)	2.5(4)	1/2
F(25)	0.4004(5)	0.4360(4)	0.1575(6)	2.1(3)	1/2

Table 4. Brief report of selected atomic distances relating to the X-ray experiment at 25 K.

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
Cu	Mn	5.450(1)	Cu	Mn	7.840(1)
Mn	O1	2.167(4)	Cu	Cu	8.221(1)
Mn	O2	2.155(3)	Cu	Mn	8.642(2)
Mn	N5	2.263(5)	Mn	Mn	8.780(1)
Mn	N6	2.266(5)	Cu	N1	1.941(4)
Mn	N7	2.278(5)	Cu	N2	1.933(5)
Mn	N8	2.257(4)	Cu	N3	2.027(4)
O1	C1	1.288(6)	Cu	N4	2.004(5)
N1	C1	1.301(8)	O2	C2	1.294(7)
C1	C2	1.532(7)	N2	C2	1.308(7)
C3	C4	1.38(1)	C4	C5	1.37(1)
C6	C7	1.49(1)	C7	C8	1.485(9)
C20	S1	1.850(8)	C21	S2	1.774(9)
C20	F11	1.33(1)	C21	F21	1.53(1)
C20	F12	1.48(1)	C21	F22	1.27(1)
C20	F13	1.33(1)	C21	F23	1.32(1)
C20	F14	1.43(1)	C21	F24	1.23(1)
C20	F15	1.24(1)	C21	F25	1.55(1)
O23	S2	1.440(5)	O13	S1	1.447(4)
O22	S2	1.440(5)	O12	S1	1.445(4)
O21	S2	1.404(8)	O11	S1	1.425(5)

Table 5. Atomic deviation distance from the mean square planes 1–3.

Atom	Distance
MnCuN1N2N3N4N5N8O1O2C1C2 (plane 1)	
Cu	−0.0035(7)
Mn	−0.0027(8)
N1	0.062(5)
N2	0.112(5)
C1	0.027(5)
C2	0.033(5)
O1	0.022(4)
O2	−0.008(4)
Mean deviation from plane is 0.03(6) Å	
MnO1O2N5N8 (plane 2)	
Mn	−0.0018(8)
N5	−0.158(5)
N8	0.186(4)
O1	−0.139(4)
O2	0.165(4)
Mean deviation from plane is 0.13(7) Å	
CuN1N2N3N4 (plane 3)	
Cu	−0.0008(7)
N1	−0.104(5)
N2	0.125(5)
N3	−0.102(5)
N4	0.113(5)
Mean deviation from plane is 0.09(9) Å	

Dihedral angles between least-squares planes: plane 2–plane 1 = 172.92°; plane 3–plane 1 = 172.63°; plane 3–plane 2 = 166.24°.

Neutron data collection and structure refinement. Neutron diffraction data were collected at 40 K at the Swedish research reactor R2 in Studsvik. The flux at the sample position was ca. 10^6 neutrons $cm^{-2}\,s^{-1}$. A double monochromator system with two copper crystals (220) was used in a parallel alignment [$\lambda = 1.215(1)$ Å]. Information concerning the data collection and structure refinement is summarized and compared with the X-ray data collection in Table 2. The cell parameters were taken from the X-ray structure determination. Three reference reflections monitored every 30 reflections showed no significant intensity (±2%). The net intensities were evaluated with the Lehmann–Larsen algorithm[8] and corrected for Lorentz and absorption effects using the experimental determined value $\mu = 2.17\ cm^{-1}$. Isotropic type I and II extinction corrections with Lorentzian mosaic distribution were applied[6] ($e_I = 0.942 \times 10^4$, $e_{II} = 0.179 \times 10^5$). The radius of a mean mosaic block is 0.218×10^{-3} cm. The neutron scattering lengths used were $b_{Cu} = 7.718$, $b_{Mn} = -3.730$, $b_C = 6.646$, $b_O = 5.803$, $b_N = 9.360$, $b_S = 2.847$, $b_F = 5.654$, and $b_H = -3.739$ fm.[9] Coordinates of the heavy atoms were taken from the 25 K X-ray model and fixed in the refinement. All hydrogen positions have been located from difference Fourier maps. After the last refinement the difference Fourier synthesis showed no significant features.

In disagreement with the nuclear structure at room temperature, we first found only 48 hydrogen atoms instead of 52 hydrogen positions in the previous report.[2] In addition the bond distances of C(3)–C(4) and C(4)–C(5) [1.38(1) and 1.37(1) Å] are close to the values expected for C=C double bonds. Because of these facts we have tried to refine three different models (A, B and C), one with single bonds and four calculated hydrogen positions, one with the two hydrogen positions found in the Fourier map and finally one with the 12 calculated or refined hydrogen positions linked two by two to the C(31), C(32), C(41), C(42), C(51) and C(52) carbon positions. The latter model gives the best fit.

The nuclear structure

The nuclear structures at 295 and 25 K appear nearly identical. The differences in the corresponding structural parameters are only those expected from a change of temperature. The structure consists of isolated $[Mn(cth)Cu(oxpn)]^{2+}$ cations and $(CF_3SO_3)_2^{2-}$ triflate anions. A view of the heterodinuclear cation is shown in Fig. 1, the two triflate anions are shown in Fig. 2.

The four nitrogen atoms of the oxpn molecule linked to the copper atom form an almost square planar group, with a mean deviation from the Cu, N(1), N(2), N(3), N(4) plane equal to 0.09(9) Å. The Cu–N(1) and Cu–N(2) lengths [1.941(4) and 1.933(5) Å, respectively] are significantly shorter than Cu–N(3) [2.027(4) Å] and Cu–N(4) [2.004(5) Å]. The manganese atom is linked to the four nitrogen atoms of the cth ligand and two oxygen

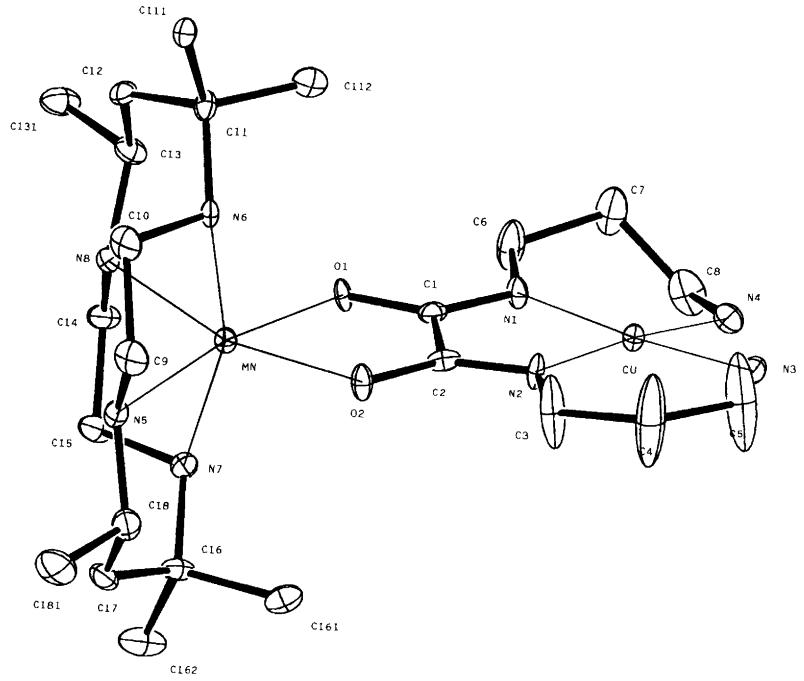

Fig. 1. Perspective view of the heterodinuclear $Mn^{II}Cu^{II}$ molecule without the hydrogen environment. (For clarification the hydrogen atoms have not been included.) Figures 1 and 2 have been drawn using ORTEP.

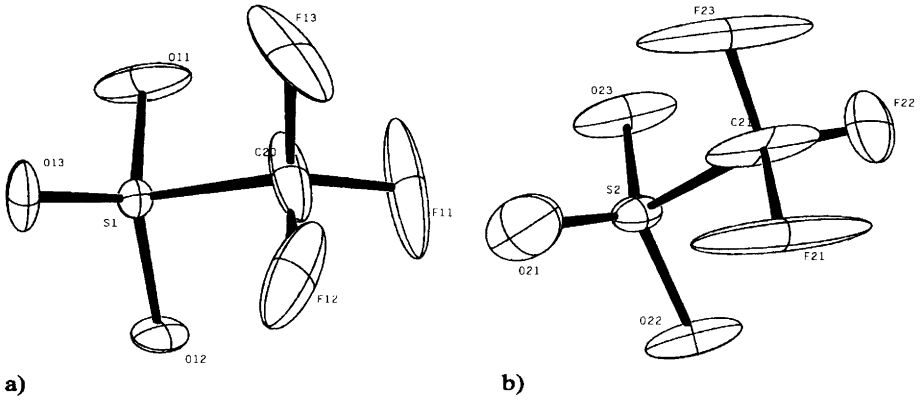

Fig. 2. Views showing the two triflate anions (a) and (b) with the very elongated ellipsoids of the fluorine atoms.

atoms of the oxamido group in a slightly distorted octahedral configuration, with an average Mn–O bond length of 2.161(4) Å and an average Mn–N bond length of 2.266(5) Å. The two metal atoms are linked by the oxamido bridge, O(1), O(2), C(1), C(2), N(1), N(2), the Mn···Cu separation being equal to 5.450(1) Å. Within the bridge the C–O average length is 1.291(7) Å and the C–N average length 1.305(8) Å showing some double bond character. On the other hand, the central C(1)–C(2) bond length, 1.532(7) Å, is characteristic for a single bond.[10]

The Mn, Cu, O(1), O(2), C(1), C(2), N(1), N(2) atoms are almost coplanar with a deviation from the mean least-squares plane of 0.03(6) Å. The dinuclear cations are well separated from each other within the lattice by the triflate ions. The shortest intermolecular metal–metal separation between two heterodinuclear molecules (Cu–Mn) is equal to 7.840(1) Å.

As mentioned above we could only find one hydrogen atom bonded to the C(3) and C(5) atoms and none to the C(4) atom in the difference Fourier maps. This is in contrast with the similar carbon positions C(6)–C(7)–C(8) on the other side of the copper ion where we found two hydrogen atoms bonded to each carbon and inconsistent with what we expect from the synthesis. The C(3)–C(4) and C(4)–C(5) distances are also much shorter than normal C–C single bonds. The thermal ellipsoids on C(3), C(4) and C(5) are more elongated compared to C(6), C(7) and C(8). This can be interpreted either as a large thermal vibration perpendicular to the bond direction or as a static disorder with two possible positions for each carbon atom. In both

cases the C–C bonds would appear to be too short. As the data collection was carried out at 25 K, the latter seems more plausible. In the final cycles we attempted to refine one model with one hydrogen atom each on C(3) and C(5) (model A), another model with six hydrogen atoms, out of which four are calculated, indicating single bonds C(3)–C(4)–C(5) (model B), as well as a model where 12 hydrogen atoms were calculated and/or refined according to the static disorder of the C(3)–C(4)–C(5) atoms (model C). The impossibility of refining the six hydrogen positions and thermal parameters according to the single bond C(3)–C(4)–C(5) lead us to fix them, whereas all hydrogen positions and thermal parameters have been refined in the model A. Except for these hydrogen positions, thermal parameters and positions for other hydrogen atoms were similar in both models. The final results gave an *R*-value of 0.083 and 0.094 for the models A and B, respectively, with the same number of reflexions used for both refinements (2864 reflexions) and the slightly different number of parameters refined (433 for model A and 415 for model B). The best result was obtained with model C, where most of the hydrogen positions were found from the Fourier map and refined, when it was possible, fixed at the calculated positions. This was the proof that the C(3)–C(4) and C(4)–C(5) bonds show a single bond character according to the synthesis instead a double bond character as supposed in the model B. This gave an *R*-value of 0.077 and a chi-square equal to 3.62 instead of 4.34 and 4.51 for models A and B, respectively.

The approximate geometry C_{3v} of the $CF_3SO_3^-$ ions could be recognized from the position of the peaks in a difference Fourier map. The C–F bond lengths differ very much depending on the model used. We have tried with three, five and six different fluorine positions for each molecule. However, the best agreement was found with five fluorine positions per molecule instead of three being extended over large regions especially for atoms F(13) and F(23). It is possible that the fluorine ends are rotating or rapidly flipping even at this low temperature. One of the two anions has been found to be more disordered than the other. At 25 K, one of the C–S bonds is longer [1.850(8) Å] whereas the other one is shorter [1.774(9) Å] than the usual value [1.83(5) Å].[10] The S–O bond distances 1.425(5), 1.445(4) and 1.447(4) Å for the first anion and 1.404(8), 1.440(5) and 1.440(5) Å for the second one are in good agreement with the characteristic S–O bond length [1.44(2) Å].

A detailed study of possible intermolecular hydrogen bonds related to the neutron experiment at 40 K has been done. From this analysis we have found only two bonds, which link the two triflate molecules to the heterodinuclear complex.[11,12] The hydrogen bonds are found to involve only one NH_2 group, namely H(3)–N(4)–H(4) with the oxygen atoms, O(22) and O(12), coming from the triflate anions. The NH···O angles are 160(2)° and 158(2)°, respectively, with N–H distances of 1.03(2) and 1.00(2) Å and H···O separations of 2.01(4) and 1.94(2) Å, respectively.

Conclusions

This investigation is an illustration of the complementarity of X-ray and neutron diffraction experiments in the frame of complicated and disordered hydrogen-bonded compounds. The results coming from the X-ray study at 25 K allowed us to determine precisely the heavy atom positions, and to describe the disordered low-temperature configuration of the triflate anions. This disorder might be assigned to a rotation or a flipping of the fluorine ends. The elongated displacement ellipsoids at the C(3)–C(4)–C(5) carbon positions have been interpreted as a static disorder with two possible positions for each carbon atom. The insertion of the heavy atom parameters in the neutron diffraction refinement has been helpful to determine the hydrogen parameters as well as to form the basis for a spin distribution study of this heterodinuclear compound.

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