

Manganese cationic pyrazolylamidino complexes

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ABSTRACT

The reactions of *fac*-[MnBr(CO)₃(NH=C(CH₃)pz^κ-κ²N,N)] (pz^κ = pz, dmpz; pzH = pyrazole; dmpzH = 3,5-dimethylpyrazole) with wet AgBF₄ in a 1:1 ratio lead to the cationic pyrazolylamidino complexes *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)pz^κ-κ²N,N)]BF₄. The aquo ligand is readily substituted by 2,6-xylylisocyanide (CNXyl) to give *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)pz^κ-κ²N,N)]BF₄. The pyrazole complexes *fac*-[Mn(pz^κH)(CO)₃(NH=C(CH₃)pz^κ-κ²N,N)]BF₄ are obtained by treating *fac*-[MnBr(CO)₃(NCMe)₂] with AgBF₄ and then with pyrazole (pzH or dmpzH), in a 1:1:2 ratio. A similar reaction using 1:1:1 ratio and AgClO₄ leads to the acetonitrile complexes *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)pz^κ-κ²N,N)]ClO₄. The X-ray structures of the complexes show moderate hydrogen bonds interactions between the N-bond hydrogen of the pyrazolylamidino ligand and the anion. In the aquo complex, one of the hydrogens of the coordinated water molecule is also involved in a hydrogen bond.

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1. Introduction

The interest of pyrazolylamidino ligands is based on several features: (a) the different properties of the two donor atoms and the electron delocalization within the ligand makes them potentially interesting for electron transfer processes and related physical properties; (b) the pyrazolylamidino ligands are synthesized in situ (Scheme 1), thus using different nitriles and pyrazoles allows the opportunity of controlling both the electronic and steric properties of the metal complexes; (c) the NH group might be deprotonated, giving rise to further reactivity. However, there are not many examples of pyrazolylamidino complexes [1], even though the amidino has been described as a promising ligand [2].

We have recently reported manganese and rhenium pyrazolylamidino neutral complexes [3]. An enhancement on the acidity of the H atom in the amidino unit should be expected for pyrazolylamidino cationic complexes. In fact, we have reported several cationic rhenium complexes, which show activity as anion receptors [3b]. Herein, we report the synthesis and structural characterization of manganese pyrazolylamidino cationic complexes.

2. Results and discussion

2.1. Syntheses of the complexes

The reactions affording to the complexes herein described are collected in Scheme 2.

The complexes *fac*-[MnBr(CO)₃(NH=C(CH₃)pz-κ²N,N)] or *fac*-[MnBr(CO)₃(NH=C(CH₃)dmpz-κ²N,N)] (pzH or 3,5-dimethylpyrazole, dmpzH) [3a] react with wet AgBF₄ in a 1:1 ratio in thf at room temperature, leading to the cationic pyrazolylamidino aquo complexes *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**1a**) or *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**1b**), respectively. The moisture present in the acetone solution of AgBF₄ is the source of the aquo ligand. The formation of carbonylmanganese(I) cationic aquo complexes is well documented in the literature [4].

When solutions of **1a** or **1b** synthesized in situ are treated with the stoichiometric amount of 2,6-xylylisocyanide (CNXyl), the aquo ligand is readily substituted by the isocyanide affording *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**2a**) and *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**2b**).

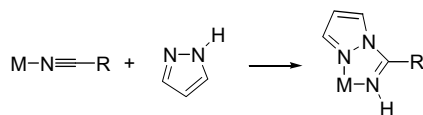
Similar pyrazole complexes *fac*-[Mn(pzH)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**3a**) and *fac*-[Mn(dmpzH)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**3b**) were obtained in a one pot process from *fac*-[MnBr(CO)₃(NCMe)₂], AgBF₄, and pyrazole (pzH or dmpzH), in a 1:1:2 ratio. Therefore, there is no need to isolate the bromopyrazolylamidino complexes, nor the aquo cationic complexes **1**, which should be intermediates in the whole process.

When similar reactions are carried out using AgClO₄ instead of AgBF₄ and 1:1:1 ratio, the incoming pyrazole prefers to become a part of the pyrazolylamidino ligand, whereas the remaining coordination site is occupied by an acetonitrile coming from the solvent, affording the complexes *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**4a**) and *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**4b**).

2.2. Solid-state structural characterization

The structure of the complexes **1b**, **2a**, **3a**, **3b**, and **4a** are shown in Figs. 1–4; whereas Tables 1–4 collect relevant distances and

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Scheme 1. General method for the synthesis of pyrazolylamidino complexes.

angles. Due to the low quality of the crystal of **2a**, the resulting determination is poor (high residuals) and contains an incipient disorder of the BF_4^- anion which could not be modelled properly. Nevertheless, the structure is included here since it confirms unambiguously the connectivity of the molecule.

The structural data of all the structures herein described are very similar to those of pyrazolylamidino ligands found in other pyrazolylamidino complexes previously reported [1], and also similar to other structures of halotricarbonylmanganese(I) complexes containing a bidentate N-donor ligand in the literature [5].

The anion and the cationic complex are linked by hydrogen bonds. Table 5 collects the strongest interactions detected. All of them may be considered as “moderate” [6]. In all the cases the hydrogen involved is the N-bond hydrogen of the pyrazolylamidino ligand, whereas in **1b**, one of the hydrogens of the coordinated water molecule is also involved.

2.3. Characterization in solution

The IR spectra of all the complexes show three bands in the C–O stretching region in solution, as expected for a *fac*-tricarbonyl geometry. The frequencies are higher than those previously reported for the parent neutral bromo complexes *fac*-[MnBr(CO)₃(NH=C(CH₃)pz-κ²N,N)] or *fac*-[MnBr(CO)₃(NH=C(CH₃)dmpz-κ²N,N)], and also slightly higher for complexes with pzH than those with dmpzH. Both features are to be expected considering the lower electronic density at the metal center in cationic vs. neutral complexes, and the better donor properties of Hdmpz compared to Hpz. The xylylisocyanide in complexes **2** show one band at ca. 2170 cm^{-1} corresponding to C–N stretching.

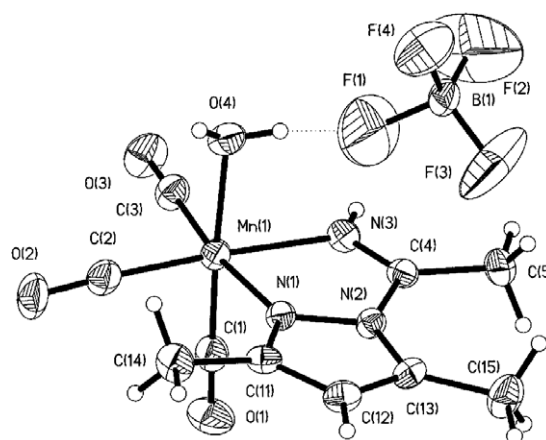
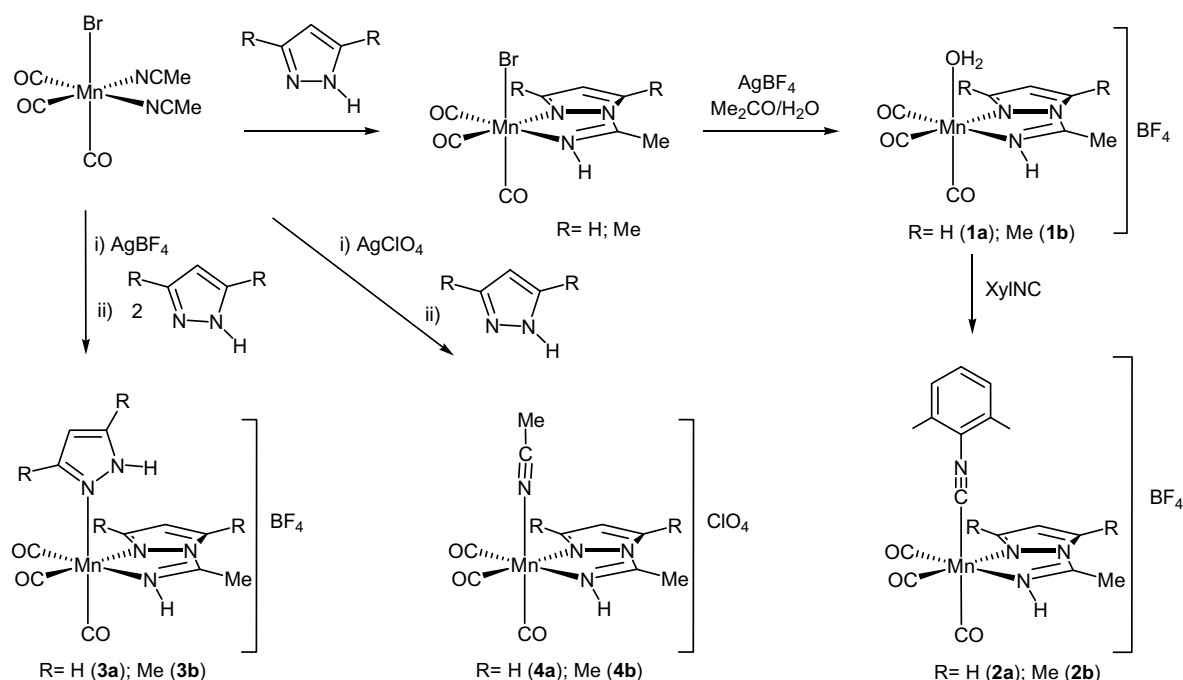


Fig. 1. Perspective view of *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**1b**) showing the atom numbering.

The ¹H and ¹³C NMR data (see Section 3) do not provide important structural information. In the spectra of complexes **3** containing both pyrazole and pyrazolylamidino ligands, the signals of the amidino fragment, both the ¹H and ¹³C NMR spectra show also higher chemical shifts respect to those reported for coordinated nitrile [7]. The signals of the aquo ligands in **1a** and **1b** in the ¹H NMR spectra are sharp singlets, suggesting the absence of exchange process between coordinated water and the solvent [8].

The ¹⁹F NMR spectra of complexes **1–3**, display a broad signal around –150 ppm corresponding to the BF₄ group. This anion usually display two singlets, respectively, assigned to ¹¹BF₄ (80%) and ¹⁰BF₄ (20%). In our case, the broadness of this signal points to a fast scrambling of the fluorine atom(s) involved in the hydrogen bonds with the cation. The broad signal does not sharpens at low temperature, indicating that this scrambling process remains fast even at low temperature. No further studies have been carried out to determine the strength of these interactions in solution, as was



Scheme 2. Syntheses of the complexes.

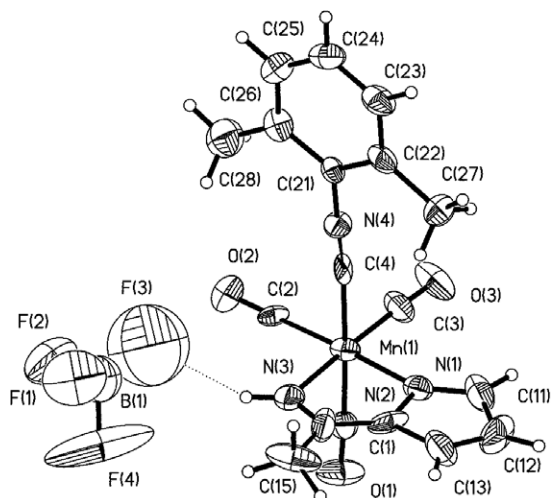


Fig. 2. Perspective view of *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**2a**) showing the atom numbering.

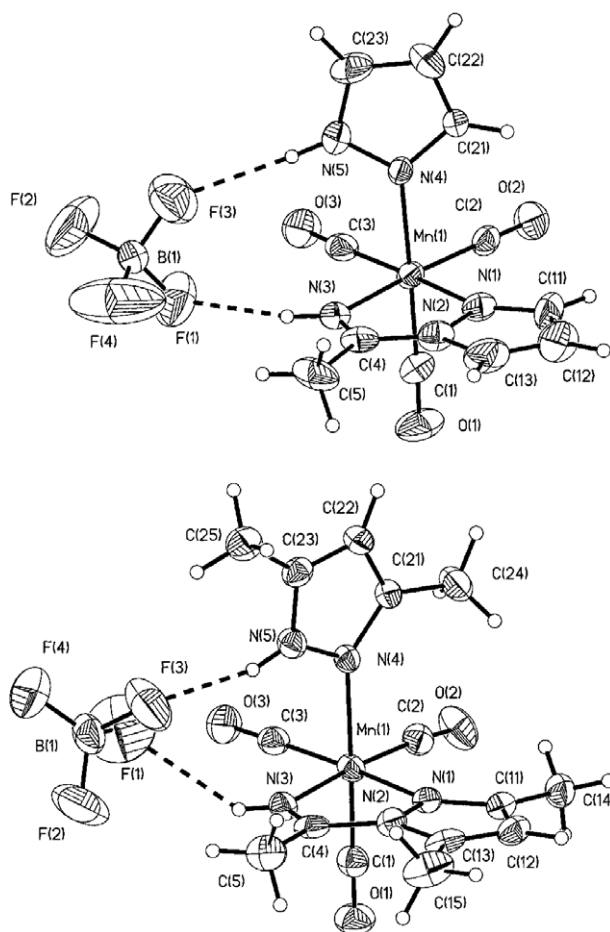


Fig. 3. Perspective views of *fac*-[Mn(pzH)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**3a**) and *fac*-[Mn(dmpzH)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**3b**) showing the atom numbering.

previously reported for similar pyrazolylamidino rhenium complexes [3b].

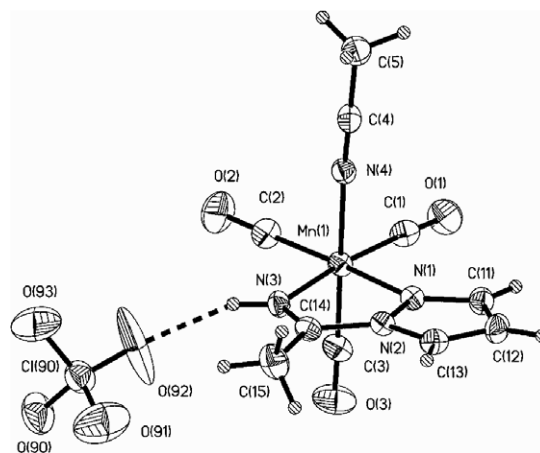


Fig. 4. Perspective view of *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)pz-κ²N,N)]ClO₄ (**4a**) showing the atom numbering.

Table 1

Selected distances (Å) and angles (°) for *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**1b**)

Mn(1)–C(1)	1.796(6)
Mn(1)–C(2)	1.810(6)
Mn(1)–C(3)	1.833(6)
Mn(1)–N(1)	2.048(4)
Mn(1)–N(3)	2.015(4)
Mn(1)–O(4)	2.108(5)
N(1)–N(2)	1.389(5)
N(2)–C(4)	1.400(6)
N(3)–C(4)	1.267(6)
C(1)–O(1)	1.132(7)
C(2)–O(2)	1.149(6)
C(3)–O(3)	1.138(6)
C(1)–Mn(1)–C(3)	89.6(2)
C(1)–Mn(1)–C(2)	88.3(2)
C(3)–Mn(1)–C(2)	89.6(2)
C(1)–Mn(1)–N(3)	91.5(2)
C(3)–Mn(1)–N(3)	95.7(2)
C(2)–Mn(1)–N(3)	174.7(2)
C(1)–Mn(1)–N(1)	92.6(2)
C(3)–Mn(1)–N(1)	171.8(2)
C(2)–Mn(1)–N(1)	98.34(19)
N(3)–Mn(1)–N(1)	76.40(16)
C(1)–Mn(1)–O(4)	177.1(2)
C(3)–Mn(1)–O(4)	91.6(2)
C(2)–Mn(1)–O(4)	94.4(2)
N(3)–Mn(1)–O(4)	85.73(19)
N(1)–Mn(1)–O(4)	85.80(16)
N(2)–N(1)–Mn(1)	113.3(3)
N(1)–N(2)–C(4)	114.4(4)
C(4)–N(3)–Mn(1)	119.8(3)

3. Experimental

3.1. General remarks

All manipulations were performed under N₂ atmosphere following conventional Schlenk techniques. Filtrations were carried out on dry Celite under N₂. Solvents were purified according to standard procedures [9]. *fac*-[MnBr(CO)₃(NH=C(CH₃)pz-κ²N,N)] and *fac*-[MnBr(CO)₃(NH=C(CH₃)dmpz-κ²N,N)] were obtained as previously described [3a]. All other reagents were obtained from the usual commercial suppliers, and used as received. CAUTION!: Although no difficulties were experienced with the perchlorate complexes described herein, all perchlorate species should be treated as potentially explosive and handled with care. Infrared spectra were recorded in Perkin–Elmer RX I FT-IR apparatus on KBr pellets

Table 2Selected distances (Å) and angles (°) for *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**2a**)

Mn(1)–C(1)	1.846(18)
Mn(1)–C(2)	1.804(18)
Mn(1)–C(3)	1.80(2)
Mn(1)–C(4)	1.972(18)
Mn(1)–N(1)	1.983(16)
Mn(1)–N(3)	2.107(17)
N(1)–N(2)	1.46(2)
N(2)–C(14)	1.28(2)
N(3)–C(14)	1.19(3)
C(1)–O(1)	1.147(17)
C(2)–O(2)	1.127(17)
C(3)–O(3)	1.155(19)
C(1)–Mn(1)–C(3)	90.6(7)
C(1)–Mn(1)–C(2)	90.5(7)
C(3)–Mn(1)–C(2)	88.4(8)
C(1)–Mn(1)–N(3)	92.2(6)
C(3)–Mn(1)–N(3)	174.5(8)
C(2)–Mn(1)–N(3)	96.2(7)
C(1)–Mn(1)–N(1)	91.1(6)
C(3)–Mn(1)–N(1)	96.9(8)
C(2)–Mn(1)–N(1)	174.4(7)
N(3)–Mn(1)–N(1)	78.3(6)
C(1)–Mn(1)–C(4)	177.9(7)
C(3)–Mn(1)–C(4)	91.3(7)
C(2)–Mn(1)–C(4)	88.6(6)
N(3)–Mn(1)–C(4)	86.0(6)
N(1)–Mn(1)–C(4)	89.7(5)
N(2)–N(1)–Mn(1)	109.0(11)
N(1)–N(2)–C(14)	118.2(18)
C(14)–N(3)–Mn(1)	113.9(16)

Table 3Selected distances (Å) and angles (°) for *fac*-[Mn(pzH)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**3a**) and *fac*-[Mn(dmpzH)(CO)₃(NH=C(CH₃)dmpz-κ²N,N)]BF₄ (**3b**)

	3a	3b
Mn(1)–C(1)	1.816(10)	1.805(8)
Mn(1)–C(2)	1.821(9)	1.803(8)
Mn(1)–C(3)	1.826(11)	1.811(9)
Mn(1)–N(1)	2.034(7)	2.053(5)
Mn(1)–N(3)	2.041(7)	2.013(5)
Mn(1)–N(4)	2.078(6)	2.117(5)
N(1)–N(2)	1.409(9)	1.386(6)
N(2)–C(4)	1.350(11)	1.395(8)
N(3)–C(4)	1.250(11)	1.270(8)
C(1)–O(1)	1.129(10)	1.141(7)
C(2)–O(2)	1.127(9)	1.154(7)
C(3)–O(3)	1.134(10)	1.136(8)
C(1)–Mn(1)–C(3)	88.9(4)	89.2(3)
C(1)–Mn(1)–C(2)	89.6(4)	85.9(3)
C(3)–Mn(1)–C(2)	88.6(4)	88.4(3)
C(1)–Mn(1)–N(3)	91.0(3)	91.6(2)
C(3)–Mn(1)–N(3)	97.7(4)	95.3(3)
C(2)–Mn(1)–N(3)	173.7(3)	175.5(3)
C(1)–Mn(1)–N(1)	92.3(3)	92.9(2)
C(3)–Mn(1)–N(1)	175.0(3)	171.4(3)
C(2)–Mn(1)–N(1)	96.3(3)	100.0(2)
N(3)–Mn(1)–N(1)	77.4(3)	76.3(2)
C(1)–Mn(1)–N(4)	177.8(3)	178.9(2)
C(3)–Mn(1)–N(4)	91.8(3)	90.3(2)
C(2)–Mn(1)–N(4)	92.5(3)	95.1(2)
N(3)–Mn(1)–N(4)	86.8(2)	87.47(19)
N(1)–Mn(1)–N(4)	86.8(3)	87.44(18)
N(2)–N(1)–Mn(1)	110.8(5)	113.3(4)
N(1)–N(2)–C(4)	118.2(7)	115.2(5)
C(4)–N(3)–Mn(1)	118.6(6)	120.2(5)

from 4000 to 400 cm⁻¹. NMR spectra were recorded in Bruker AC-300 or ARX-300 instruments in (CD₃)₂CO, at room temperature unless otherwise stated. NMR spectra are referred to the internal residual solvent peak for ¹H and ¹³C{¹H} NMR. Assignment of the

Table 4Selected distances (Å) and angles (°) for *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)pz-κ²N,N)]ClO₄ (**4a**)

Mn(1)–C(1)	1.798(6)
Mn(1)–C(2)	1.806(5)
Mn(1)–C(3)	1.799(6)
Mn(1)–N(1)	2.017(4)
Mn(1)–N(3)	2.029(4)
Mn(1)–N(4)	2.016(4)
N(1)–N(2)	1.364(4)
N(2)–C(4)	1.401(5)
N(3)–C(4)	1.259(5)
C(1)–O(1)	1.136(6)
C(2)–O(2)	1.133(5)
C(3)–O(3)	1.151(6)
C(1)–Mn(1)–C(3)	89.5(2)
C(1)–Mn(1)–C(2)	88.6(2)
C(3)–Mn(1)–C(2)	92.9(2)
C(1)–Mn(1)–N(3)	90.97(18)
C(3)–Mn(1)–N(3)	94.74(19)
C(2)–Mn(1)–N(3)	172.37(18)
C(1)–Mn(1)–N(1)	93.83(19)
C(3)–Mn(1)–N(1)	170.98(18)
C(2)–Mn(1)–N(1)	95.57(18)
N(3)–Mn(1)–N(1)	76.85(14)
C(1)–Mn(1)–N(4)	178.94(19)
C(3)–Mn(1)–N(4)	91.3(2)
C(2)–Mn(1)–N(4)	92.02(19)
N(3)–Mn(1)–N(4)	88.31(15)
N(1)–Mn(1)–N(4)	85.25(14)
N(2)–N(1)–Mn(1)	113.5(3)
N(1)–N(2)–C(4)	116.7(3)
C(4)–N(3)–Mn(1)	119.4(3)

Table 5Hydrogen bonds detected in the crystal structures of **1b**, **2a**, **3a**, **3b**, and **4a**

1b	H(4B)···(1) 1.908 Å	O(4)···F(1) 2.686 Å
1b	H(3)···F(4) 2.230 Å ^a	N(3)···F(4) 2.995 Å ^a
2a	H(3)···F(3) 2.227 Å	N(3)···F(3) 3.003 Å
3a	H(3)···F(1) 2.233 Å	N(3)···F(1) 3.063 Å
3a	H(5)···F(3) 2.257 Å	N(5)···F(3) 3.085 Å
3b	H(3)···F(1) 2.448 Å	N(3)···F(1) 3.169 Å
3b	H(5)···F(3) 2.104 Å	N(5)···F(3) 2.898 Å
4a	H(3)···O(92) 2.127 Å	N(3)···O(92) 2.917 Å

^a This interaction is not displayed in Fig. 1 since F(4) belongs to another BF₄⁻ anion not depicted in the figure.

¹³C{¹H} NMR data was supported by DEPT experiments and relative intensities of the resonance signals. Elemental analyses were performed on a Perkin–Elmer 2400B microanalyzer.

3.2. *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)pz-κ²N,N)]BF₄ (**1a**)

To a solution of *fac*-[MnBr(CO)₃(NH=C(CH₃)pz-κ²N,N)], (0.131 g, 0.4 mmol) in thf (10 mL), a 0.1 M solution of AgBF₄ in wet acetone (4 mL, 0.4 mmol) was added. The mixture was stirred at room temperature excluded from the sunlight for 30 min, and the volatiles were removed in vacuo and the yellow residue was extracted with thf (ca. 20 mL) and filtered. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to –20 °C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.102 g (72%) of **1a**. IR (thf, cm⁻¹): 2044 vs, 1948 vs, 1936 vs. IR (KBr, cm⁻¹): 3444 m, 3153 w, 2054 s, 1957 vs, 1940 vs br, 1657 m, 1537 w, 1465 w, 1408 s, 1336 w, 1250 w, 1133 s, 1046 s, 1002 s, 768 w, 631 m, 514 w. ¹H NMR (Me₂CO-*d*₆): 2.90 (s, N=C(CH₃), 3H), 4.76 (s, OH₂, 2H), 6.92 (s, H⁴ pz, 1H), 8.63 (br s, H³ pz, 1H), 8.73 (br s, H⁵ pz, 1H), 10.97 (br, HN, 1H). ¹³C{¹H} NMR (Me₂CO-*d*₆): 18.8 (s, HN=C(CH₃)), 113.0 (s, C⁴ pz), 135.0 (s,

$C^{3,5}$ pz), 149.6 (s, $C^{5,3}$ pz), 166.3 (s, $HN=C(CH_3)$), 219.1 (s, CO), 220.1 (s, CO), 221.6 (s, CO). ^{19}F NMR (Me_2CO-d_6): -148.1 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_8H_9BF_4MnN_3O_4$: C, 27.23; H, 2.57; N, 11.91. Found: C, 26.89; H, 2.36; N, 11.69%.

3.3. *fac*-[Mn(OH₂)(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)]BF₄ (**1b**)

To a solution of *fac*-[MnBr(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)] (0.036 g, 0.1 mmol) in thf (10 mL), a 0.17 M solution of AgBF₄ in wet acetone (0.60 mL, 0.1 mmol) was added. The mixture was stirred at room temperature excluded from the sunlight for 30 min, and the volatiles were removed in vacuo. The yellow residue was extracted with CH₂Cl₂ (ca. 20 mL) and filtered. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to -20 °C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.097 g (51%) of **1b**. IR (thf, cm^{-1}): 2040 vs, 1940 vs, 1934 vs. IR (KBr, cm^{-1}): 3448 m, 3327 m, 2048 vs, 1956 vs, 1924 vs, 1647 m, 1575 w, 1453 w, 1416 m, 1356 w, 1251 w, 1100 s, 1048 s, 829 w, 639 w, 514 w. 1H NMR (Me_2CO-d_6): 2.69 (s, CH_3 dmpz, 3H), 2.71 (s, CH_3 dmpz, 3H), 2.98 (s, $N=C(CH_3)$, 3H), 4.72 (s, OH_2 , 2H), 6.57 (s, H^4 dmpz, 1H), 10.80 (br, HN , 1H). $^{13}C\{^1H\}$ NMR (Me_2CO-d_6): 14.1 (s, CH_3 dmpz), 15.3 (s, CH_3 dmpz), 21.4 (s, $HN=C(CH_3)$), 115.1 (s, C^4 dmpz), 147.4 (s, $C^{3,5}$ dmpz), 159.2 (s, $C^{5,3}$ dmpz), 167.7 (s, $HN=C(CH_3)$), 219.9 (s, CO), 220.7 (s, CO), 221.2 (s, CO). ^{19}F NMR (Me_2CO-d_6): -148.1 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_{10}H_{13}BF_4MnN_3O_4$: C, 31.53; H, 3.40; N, 11.03. Found: C, 31.84; H, 3.10; N, 10.91%.

3.4. *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)pz- κ^2 N,N)]BF₄ (**2a**)

A recently prepared solution of **1a** (starting from 0.098 g, 0.3 mmol of *fac*-[MnBr(CO)₃(NH=C(CH₃)pz- κ^2 N,N)] in thf (10 mL) was synthesized as described above. After filtering to remove AgBr, CNXyl (0.039 g, 0.3 mmol) was added and the solution was stirred at room temperature for 5 h. Hexane was added (ca. 10 mL) and the solution was concentrated and cooled to -20 °C, giving a pale yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.098 g (70%) of **2a**. IR (thf, cm^{-1}): 2171 w, 2048 vs, 1985 s, 1955 vs. IR (KBr, cm^{-1}): 3311 w, 2172 m, 2045 vs, 1979 s, 1951 s, 1654 m, 1083 s, 786 w, 628 w. 1H NMR (Me_2CO-d_6): 2.24 (s, $CNC_6H_3(CH_3)_2$, 6H), 2.93 (s, $N=C(CH_3)$, 3H), 6.98 (s, H^4 pz, 1H), 7.20 and 7.28 (AB₂ system, $CNC_6H_3(CH_3)_2$, 3 H), 8.57 (d, $J = 1.2$ Hz, H^3 pz, 1H), 8.85 (d, $J = 3.1$ Hz, H^5 pz, 1H), 10.73 (br, HN , 1H). $^{13}C\{^1H\}$ NMR (Me_2CO-d_6): 18.2 (s, $CNC_6H_3(CH_3)_2$), 18.9 (s, $HN=C(CH_3)$), 113.5 (s, C^4 dmpz), 127.1 (s, C_{ipso} $CNC_6H_3(CH_3)_2$), 128.9 (s, *meta*- $CNC_6H_3(CH_3)_2$), 130.7 (s, *para*- $CNC_6H_3(CH_3)_2$), 135.1 (s, $C^{3,5}$ pz), 136.1 (s, *ortho*- $CNC_6H_3(CH_3)_2$), 150.2 (s, $C^{5,3}$ pz), 164.6 (s, $HN=C(CH_3)$), 206.5 (s, CNXyl), 218.7 (br s, CO). ^{19}F NMR (Me_2CO-d_6): -148.8 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_{17}H_{16}BF_4MnN_4O_3$: C, 43.81; H, 3.46; N, 12.02. Found: C, 43.52; H, 3.31; N, 11.85%. X-ray diffraction: high values for residuals R_{int} , R and wR_2 are obtained due to the low quality of the crystal.

3.5. *fac*-[Mn(CNXyl)(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)]BF₄ (**2b**)

A recently prepared solution of **1b** (starting from 0.071 g, 0.2 mmol of *fac*-[MnBr(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)] in thf (10 mL) was synthesized as described above. After filtering to remove AgBr, CNXyl (0.026 g, 0.2 mmol) was added and the solution was stirred at room temperature for 5 h. Work-up as for **2a** gave 0.088 g (90%) of **2b** as a pale yellow microcrystalline solid. IR (thf, cm^{-1}): 2169 w, 2046 vs, 1983 s, 1948 s. IR (KBr, cm^{-1}): 3338 m, 3318 w, 2179 s, 2045 vs, 1982 vs, 1946 vs, 1655 m, 1575 m, 1478 m, 1452 s, 1412 s, 1355 m, 1246 w, 1073 vs, 786

m, 674 m, 636 s. 1H NMR (Me_2CO-d_6): 2.27 (s, $CNC_6H_3(CH_3)_2$, 6 H), 2.66 (s, CH_3 dmpz, 3H), 2.73 (s, CH_3 dmpz, 3H), 2.99 (s, $N=C(CH_3)$, 3H), 6.61 (s, H^4 dmpz, 1H), 7.23 and 7.31 (AB₂ system, $CNC_6H_3(CH_3)_2$, 3H), 10.48 (br, HN , 1H). $^{13}C\{^1H\}$ NMR (Me_2CO-d_6): 14.2 (s, CH_3 dmpz), 15.4 (s, CH_3 dmpz), 18.2 (s, $CNC_6H_3(CH_3)_2$), 21.5 (s, $HN=C(CH_3)$), 115.4 (s, C^4 dmpz), 128.9 (s, *meta*- $CNC_6H_3(CH_3)_2$), 129.2 (s, *para*- $CNC_6H_3(CH_3)_2$), 130.7 (s, C_{ipso} $CNC_6H_3(CH_3)_2$), 136.1 (s, *ortho*- $CNC_6H_3(CH_3)_2$), 147.9 (s, $C^{3,5}$ dmpz), 159.6 (s, $C^{5,3}$ dmpz), 166.3 (s, $HN=C(CH_3)$), CNXyl and CO not observed. ^{19}F NMR (Me_2CO-d_6): -150.2 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_{19}H_{20}BF_4MnN_4O_3$: C, 46.18; H, 4.08; N, 11.34. Found: C, 45.93; H, 3.98; N, 11.02%.

3.6. *fac*-[Mn(pzH)(CO)₃(NH=C(CH₃)pz- κ^2 N,N)]BF₄ (**3a**)

A solution of [MnBr(CO)₅] (0.083 g, 0.3 mmol) in CH₃CN (10 mL) was maintained at 60 °C for 30 min. Then a 0.1 M solution of AgBF₄ in wet acetone (3.3 mL, 0.33 mmol) was added, and the mixture was stirred at 40 °C excluded from the sunlight for 1 h. Then pzH (0.041 g, 0.6 mmol) was added and the mixture was refluxed during 18 h. Work-up as for **1b** gave 0.053 (44%) of **3a** as yellow crystals. IR (thf, cm^{-1}): 2043 vs, 1951 s, 1940 vs. IR (KBr, cm^{-1}): 3336 s, 3141 m, 2042 vs, 1956 vs, 1929 vs, 1655 s, 1535 m, 1464 m, 1406 s, 1242 m, 1118 m, 1084 s, 1052 s, 760 s, 633 m. 1H NMR (Me_2CO-d_6): 2.94 (s, $N=C(CH_3)$, 3 H), 6.42 (d, $J = 1.9$ Hz, H^4 pzH, 1H), 6.95 (pst, $J = 2.5$ Hz, H^4 pz, 1H), 7.57 (pst, $J = 1.9$ Hz, H^3 pzH, 1H), 7.90 (d, $J = 1.9$ Hz, H^5 pzH, 1H), 8.70 (d, $J = 1.9$ Hz, H^3 pz, 1H), 8.73 (d, $J = 2.5$ Hz, H^5 pz, 1H), 10.93 (br, $HN=C(CH_3)$, 1H), 12.44 (br, HN pzH, 1H). $^{13}C\{^1H\}$ NMR (Me_2CO-d_6): 19.0 (s, $HN=C(CH_3)$), 108.0 (s, C^4 pzH), 113.3 (s, C^4 pz), 133.8 (s, $C^{3,5}$ pzH), 135.0 (s, $C^{3,5}$ pz), 144.1 (s, $C^{5,3}$ pzH), 149.9 (s, $C^{5,3}$ pz), 165.7 (s, $HN=C(CH_3)$), 219.6 (br s, CO). ^{19}F NMR (Me_2CO-d_6): -148.1 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_{11}H_{11}BF_4MnN_5O_3$: C, 32.79; H, 2.75; N, 17.38. Found: C, 33.02; H, 2.43; N, 17.09%.

3.7. *fac*-[Mn(dmpzH)(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)]BF₄ (**3b**)

A solution of [MnBr(CO)₅] (0.083 g, 0.3 mmol) in CH₃CN (10 mL) was maintained at 60 °C for 30 min. Then a 0.1 M solution of AgBF₄ in wet acetone (3.3 mL, 0.33 mmol) was added, and the mixture was stirred at 40 °C excluded from the sunlight for 1 h. Then dmpzH (0.041 g, 0.6 mmol) was added and the mixture was refluxed during 18 h. Work-up as for **1b** gave 0.069 (50%) of **3b** as yellow crystals. IR (thf, cm^{-1}): 2039 s, 1949 s, 1931 vs. IR (KBr, cm^{-1}): 3402 m, 3352 m, 2036 vs, 1942 vs, 1926 vs, 1642 m, 1577 m, 1419 s, 1101 s, 1044 s, 812 m, 645 w, 522 w. 1H NMR (Me_2CO-d_6): 2.18 (s, CH_3 dmpzH, 3H), 2.23 (s, CH_3 dmpzH, 3H), 2.65 (s, CH_3 dmpz, 3H), 2.74 (s, CH_3 dmpz, 3H), 2.92 (s, $N=C(CH_3)$, 3 H), 5.97 (s, H^4 dmpzH, 1H), 6.55 (s, H^4 dmpz, 1H), 10.41 (br, $HN=C(CH_3)$, 1H), 10.93 (br, HN dmpzH, 1H). $^{13}C\{^1H\}$ NMR (Me_2CO-d_6): 10.5 (s, CH_3 dmpzH), 14.2 (s, CH_3 dmpz), 14.5 (s, CH_3 dmpzH), 15.8 (s, CH_3 dmpz), 21.5 (s, $HN=C(CH_3)$), 108.1 (s, C^4 dmpzH), 115.2 (s, C^4 dmpz), 144.5 (s, $C^{3,5}$ dmpzH), 148.3 (s, $C^{3,5}$ dmpz), 154.3 (s, $C^{5,3}$ dmpzH), 160.0 (s, $C^{5,3}$ dmpz), 167.5 (s, $HN=C(CH_3)$), 220.1 (br s, CO). ^{19}F NMR (Me_2CO-d_6): -148.0 (br, $^{10}BF_4$, 4F and $^{11}BF_4$, 4F). Anal. Calc. for $C_{15}H_{19}BF_4MnN_5O_3$: C, 39.24; H, 4.17; N, 15.25. Found: C, 39.24; H, 3.89; N, 14.93%.

3.8. *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)pz- κ^2 N,N)]ClO₄ (**4a**)

A solution of [MnBr(CO)₅] (0.137 g, 0.5 mmol) in CH₃CN (20 mL) was maintained at 60 °C for 30 min. Then AgClO₄ (0.114 g, 0.55 mmol) was added, and the mixture was stirred at 60 °C excluded from the sunlight for 1 h. Then pzH (0.034 g, 0.5 mmol) was added and the mixture was refluxed during 18 h. Work-up as for **1b** gave 0.115 g (59%) of **4a** as yellow crystals. IR (thf,

Table 6
Crystal data and refinement details for **1a**, **2a**, **3a**, **3b**, and **4a**

	1b	2a	3a	3b	4a
Formula	C ₁₀ H ₁₃ BF ₄ MnN ₃ O ₄	C ₁₇ H ₁₆ BF ₄ MnN ₄ O ₃	C ₂₂ H ₂₂ B ₂ F ₈ Mn ₂ N ₁₀ O ₆	C ₁₅ H ₁₉ BF ₄ MnN ₅ O ₃	C ₁₀ H ₁₀ ClMnN ₄ O ₇
Formula weight	380.98	466.09	806.00	459.10	388.61
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 1	<i>P</i> 2(1)2(1)2(1)	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	8.336(5)	7.824(8)	12.807(3)	13.238(3)	6.725(3)
<i>b</i> (Å)	9.223(5)	8.664(9)	15.698(4)	11.694(2)	14.457(7)
<i>c</i> (Å)	20.929(11)	15.884(16)	16.442(4)	13.667(3)	16.453(8)
α (°)	90	99.992(13)	90	90	90
β (°)	99.417(9)	96.31(2)	90	106.809(4)	101.364(11)
γ (°)	90	91.93(2)	90	90	90
<i>V</i> (Å ³)	1587.3(15)	1052.4(18)	3305.7(13)	2025.2(7)	1568.2(14)
<i>Z</i>	4	2	4	4	4
<i>T</i> (K)	296(2)	293(2)	298(2)	298(2)	293(2)
<i>D</i> _{calc} (g cm ⁻³)	1.594	1.471	1.619	1.506	1.646
<i>F</i> (000)	768	472	1616	936	784
λ (Mo <i>K</i> α) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size (mm); color	0.43 × 0.14 × 0.09; yellow	0.39 × 0.12 × 0.05; pale yellow	0.22 × 0.14 × 0.09, yellow	0.27 × 0.08 × 0.03, yellow	0.21 × 0.06 × 0.03; yellow
μ (mm ⁻¹)	0.893	0.687	0.862	0.714	1.052
Scan range (°)	1.97 ≤ θ ≤ 23.32	1.31 ≤ θ ≤ 23.16	1.79 ≤ θ ≤ 23.30	1.61 ≤ θ ≤ 23.31	1.89 ≤ θ ≤ 23.30
Absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS
Corr. factors (maximum, minimum)	1.000000, 0.825580	1.000000, 0.12755	1.000000, 0.723207	1.000000, 0.510039	1.000000, 0.746960
Number of measured reflection	6877	4337	21570	12937	6862
Number of independent reflection [<i>R</i> _{int}]	2295 [0.0246]	2837 [0.2655]	4768 [0.1300]	2913 [0.1016]	2254 [0.0444]
<i>I</i> ≥ 2 σ (<i>I</i>)	1856	1234	3404	1638	2254
Goodness-of-fit (GOF) of <i>F</i> ²	1.086	1.223	1.027	1.002	0.985
Number of parameters	223	250	453	267	210
Residuals <i>R</i> , <i>wR</i> ₂	0.0583, 0.1709	0.1487, 0.4259	0.0692, 0.1785	0.0661, 0.2019	0.0430, 0.1175

cm⁻¹): 2042 s, 1947 s, 1932 vs. IR (KBr, cm⁻¹): 3276 w, 2051 s, 1978 s, 1951 vs, 1664 w, 1410 m, 1090 s, 776 w, 624 w. ¹H NMR (Me₂CO-*d*₆): 2.29 (s, NCCH₃, 3 H), 2.95 (s, N=C(CH₃), 3 H), 6.94 (s, H⁴ pz, 1H), 8.53 (s, H³ pz, 1H), 8.77 (s, H⁵ pz, 1H), 10.87 (br, HN, 1H). ¹³C{¹H} NMR (Me₂CO-*d*₆): 3.2 (s, NCCH₃), 19.1 (s, HN=C(CH₃)), 113.1 (s, C⁴ pz), 127.8 (s, NCCH₃), 135.1 (s, C^{3,5} pz), 149.5 (s, C^{5,3} pz), 165.5 (s, HN=C(CH₃)), CO not observed. Anal. Calc. for C₁₀H₁₀ClMnN₄O₇: C, 30.91; H, 2.59; N, 14.42. Found: C, 30.98; H, 2.33; N, 14.39%.

3.9. *fac*-[Mn(NCMe)(CO)₃(NH=C(CH₃)dmpz- κ^2 N,N)]ClO₄ (**4b**)

A solution of [MnBr(CO)₅] (0.137 g, 0.5 mmol) in CH₃CN (20 mL) was maintained at 60 °C for 30 min. Then AgClO₄ (0.114 g, 0.55 mmol) was added, and the mixture was stirred at 60 °C excluded from the sunlight for 1 h. Then dmpzH (0.048 g, 0.5 mmol) was added and the mixture was refluxed during 18 h. Work-up as for **1b** gave 0.125 g (60%) of **4b** as yellow crystals. IR (thf, cm⁻¹): 2039 vs, 1940 vs, 1932 vs. IR (KBr, cm⁻¹): 3301 m, 2047 vs, 1965 vs, 1953 vs, 1940 vs, 1647 m, 1575 m, 1456 m, 1416 m, 1358 m, 1245 w, 1092 s, 624 m. ¹H NMR (Me₂CO-*d*₆): 2.30 (s, NCCH₃, 3H), 2.63 (s, CH₃ dmpz, 3H), 2.70 (s, CH₃ dmpz, 3H), 2.98 (s, N=C(CH₃), 3H), 6.54 (s, H⁴ dmpz, 1H), 10.78 (br, HN, 1 H). ¹³C{¹H} NMR (Me₂CO-*d*₆): 3.2 (s, NCCH₃), 14.2 (s, CH₃ dmpz), 15.2 (s, CH₃ dmpz), 21.6 (s, HN=C(CH₃)), 115.1 (s, C⁴ dmpz), 127.5 (s, NCCH₃), 147.6 (s, C^{3,5} dmpz), 158.8 (s, C^{5,3} dmpz), 167.0 (s, HN=C(CH₃)), 217.6 (s, CO), 219.8 (s, CO). Anal. Calc. for C₁₂H₁₄ClMnN₄O₇: C, 34.59; H, 3.39; N, 13.45. Found: C, 34.24; H, 3.34; N, 13.36%.

3.10. X-ray crystallographic study of **1b**, **2a**, **3a**, **3b** and **4a**

Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH₂Cl₂ at -20 °C. Relevant crystallographic details are given in Table 6. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 dif-

fractometer with graphite monochromatized Mo *K* α X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6^\circ$. Raw frame data were integrated with the SAINT program [10]. The structure was solved by direct methods with SHELXTL [11]. A semi-empirical absorption correction was applied with the program SADABS [12]. All non-hydrogen atoms were refined anisotropically except for the low quality structure of **2a**, in which some atoms had to be refined isotropically to avoid non-positive-definite ellipsoids. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL.

4. Supplementary data

CCDC 685546, 685547, 685548, 685549 and 685550 contain the supplementary crystallographic data for **1a**, **2a**, **3a**, **3b** and **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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