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Synthesis, Characterization and Magnetic Behaviour of Tetra-μ_3-fluorododecakis-(5-methylpyrazole-N^2)tetrametal(II) Tetrakis(tetrafluoroborates)

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3(5)-Methylpyrazole (3(5)-MPZ) was found to induce tetrafluoroborate decomposition upon the reaction with $M(BF_4)_2\cdot aq$ salts, yielding fluoride containing compounds, analysing as $MF(5\text{-}MPZ)_3(BF_4)$. For M = Cd and Mn this reaction proceeds at room temperature, while for M = Co and Ni higher reaction temperatures (up to 80 °C) have to be used. According to IR, UV and EPR spectroscopy and X-ray powder diagrams a tetrameric structure is proposed in correspondence to the known structure of $[Co_4F_4(N\text{-}ethylimidazole)_{12}](BF_4)_4$.

The ligand 3(5)-MPZ is believed to bind to the metals with the methyl substituent in the 5-position. Magnetic susceptibility studies down to 2 K indicate weak antiferromagnetic interaction between the metal ions in the cluster. The magnitude of the exchange parameter for the Co-compound ($J/k \approx -7$ K) is comparable to the one found previously for $Co_4F_4(N\text{-}ethylimidazole)_{12}(BF_4)_4$.

Introduction

Some years ago it was discovered that metal fluoride compounds can easily be obtained from metal tetrafluoroborates [1–3]. Depending both on the type of ligand and solvent used and on the reaction temperatures, decomposition of the tetrafluoroborate anion occurs, giving BF_3 (most likely being coordinated to ligand or solvent molecules) and a fluoride anion, which is transferred to the metal center.

Since the first reports several examples of fluoride complexes, synthesized via the BF_4^- decomposition reaction, have been reported [4–11]. Besides monomeric metal fluoride compounds MF_2L_4 (M = Ni, Co, Zn or Cd, L = 4-hydroxypyridine [5]) and $MF_2L_4(BF_4)$ (M = Cr, L = 3(5)-MPZ [6]), fluoride bridged dimers $M_2F_2L_n$ (M = Co, L = 3,5-dimethylpyrazole [7], lutidine-N-oxide [9], n = 6; M = Cu, L = 1:2 mixture of 3,5-dimethylpyrazole and 5-MPZ [12], n = 6; M = Fe, Co, Ni, Cd or Cu, L = bis(3,5-methylpyrazolyl)methane [8, 11], n = 4), cubane-like tetramers $M_4F_4L_{12}(BF_4)_4$ (M = Co, Cd or Mn, L = N-ethylimidazole or N-propylimidazole [10]) and linear chain compounds MF_2L_2 (M = Co, Cd, Mn, Cu, Zn or Ni, L = 3,5-dimethylpyrazole [3, 12]) have been isolated.

The objective for the synthesis of metal fluoride coordination compounds is not only based on the aim to explore the synthetic applicability of the fluoride transfer reaction and the structural details of the compounds, but also on current interest in the magnetic-exchange interaction in halogen bridged metal assemblies. Recent results obtained for fluoride bridged dimeric and tetrameric complexes show that relatively small antiferromagnetic interactions ($T(\chi_{max}) < 30$ K) may be expected [8, 10, 11, 13].

In this paper we describe the results of the reactions of 3(5)-MPZ with metal tetrafluoroborates, giving further examples of the fluoride transfer reactions as a route to the synthesis of new polynuclear fluoride bridged compounds which show relatively small exchange interactions.

Experimental

Starting Materials

3(5)-MPZ was used as obtained from Aldrich-Europe. The cadmium and manganese tetrafluoroborates were prepared using the reaction of the corresponding metal carbonates with tetrafluoroboric acid (35% in water). For the reaction with 3(5)-MPZ these metal tetrafluoroborates were used as their solutions in water.

Hexakis(5-methylpyrazole)nickel and -cobalt bis(tetrafluoroborates) were prepared according to published methods [14].

Synthesis of the Compounds $M_4F_4(5\text{-}MPZ)_{12}(BF_4)_4$

M = Cd and Mn (complex I and II respectively)

3(5)-MPZ (30 mmol) was added to an ethanolic solution (10 ml) of $M(BF_4)_2\cdot aq$ (4 mmol) containing

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TABLE I. Analytical and Physical Data of Compounds with General Formula $M_4F_4(5\text{-}MPZ)_{12}(BF_4)_4$.

M	Colour	%M	%C	%H	%N	%F	M.p. (°C)
Cd	white	23.1(24.2)[a]	30.98(31.02)	4.04(3.91)	17.3(18.1)	20.8(20.5)	198–200
Mn	white	13.0(13.5)	36.02(35.40)	4.81(4.47)	19.7(20.7)	23.4(23.2)	>250
Co	rose	14.1(14.3)	35.51(35.06)	4.64(4.42)	20.0(20.5)	23.3(23.1)	184–186
Ni	light green	13.8(14.3)	35.09(35.07)	4.76(4.42)	18.5(20.5)	23.2(23.1)	244–245

[a] Calculated values in parentheses.

triethylorthoformate (5 ml) for dehydration [15]. Addition, after a few minutes, of diethyl ether resulted in the precipitation of white solids of the compounds I and II. These were isolated by filtration, washed with diethyl ether and dried *in vacuo*.

M = Co and Ni (complex III and IV respectively)

Complexes $M(5\text{-}MPZ)_6(BF_4)_2$ (5 mmol) were heated in ethanol or tetrahydrofuran (400 ml) at reflux temperatures for about three hours. Light green and pink precipitates of III and IV were formed respectively. Isolation was performed by filtration, washing with diethyl ether and drying *in vacuo*.

Compounds I–IV were recrystallised from ethanol/ diethyl ether mixtures, yielding octahedrally shaped crystals. Unfortunately, single crystals suitable for X-ray analysis could not be obtained. For M = Mn and Co crystalline by-products free of BF_4^- were obtained during the preparations, analysing as MF_2-$(5\text{-}MPZ)_n$ (n = 2–4). The detailed nature of these compounds is subject of further investigations.

Analyses and Measurements

Metal contents were determined by standard EDTA titrations, while C, H, N and F analyses were carried out by the Mikroanalytisches Laboratorium of E. Pascher, Buschstrasse 54, 5300 Bonn 1, F.R.G. Infrared spectra in the range 4000–180 cm^{-1} were recorded on a model 580 Perkin-Elmer infrared spectrometer, using Nujol mulls. UV–visible spectra were obtained with a Beckman DK-2A ratio recording spectrophotometer (range 35,000–4000 cm^{-1}) by using the diffuse reflectance technique, with MgO as a reference. X-band EPR spectra were measured on a Varian E-3 spectrometer at room and liquid nitrogen temperatures, using powdered samples.

X-ray powder diagrams were obtained with a Guinier–de Wolff type powder camera, using Cu-Kα radiation. The samples were mounted on adhesive tape.

The magnetic susceptibility measurements (2–90 K) were carried out using a parallel field vibrating sample magnetometer (PAR model 150A) with a Janis cryostat, equipped with a Westinghouse superconducting magnet [16].

Results and Discussion

General

The first report concerning the reactions of metal tetrafluoroborates with 3(5)-MPZ described the formation of complexes with the general formula $M(5\text{-}MPZ)_n(BF_4)_2$ (M = Co or Ni, n = 6; M = Cu, n = 4) [14]. However, it was observed that the cadmium and manganese complexes of this type could not be obtained, at least not pure [14]. A re-examination of the reaction with the cadmium and manganese tetrafluoroborate now reveals that decomposition of one half of the BF_4^- anions takes place with the concomitant transfer of fluoride anions to the metal center, resulting in crystalline products with formula $M_4F_4(5\text{-}MPZ)_{12}(BF_4)_4$ (I: M = Cd; II: M = Mn).

Obviously, the Cd and Mn complexes of the type $M(5\text{-}MPZ)_n(BF_4)_2$ are thermally not stable at room temperature, in contrast to the corresponding Co and Ni compounds. Nevertheless, if these latter compounds are heated in refluxing ethanol or tetrahydrofuran, similar decomposition of the BF_4^- ion occurs, followed by the formation of compounds $M_4F_4(5\text{-}MPZ)_{12}(BF_4)_4$ (III: M = Co; IV: M = Ni).

The results of elemental analysis, summarized in Table I, confirm the proposed stoichiometry.

X-ray Data

Recent X-ray structure determinations have shown that metal fluoride compounds having a MFL_3^+ stoichiometry may have either a dimeric (*e.g.* Co_2F_2-$(3,5\text{-dimethylpyrazole})_6(BF_4)_2$ [7]) or a tetrameric structure (*e.g.* $Co_4F_4(N\text{-ethylimidazole})_{12}(BF_4)_4$ [10] in which the metal atoms are five (A) and six (B) coordinated respectively. Even for the neutral compound $(Mn_4(CO)_{12}F_x(OH)_{4-x})$ with a MFL_3 stoichiometry, a cubane-like tetranuclear structure containing triple-bridging fluoride anions has been found [17].

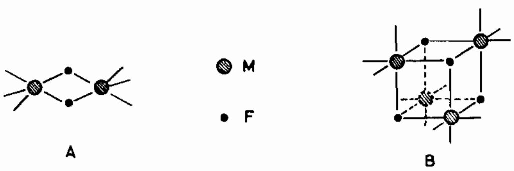
The factors that will finally determine the actual structure are thought to be primarily steric.

In the absence of single-crystal data, information about the structure of the compounds I–IV has been

TABLE II. d-Values for Compounds of the Type $M_4F_4L_{12}(BF_4)_4$, Obtained from Guinier–de Wolff Powder Diagrams Using Cu-Kα Radiation. The ten most intense lines are summarized.

L = N-ethylimidazole M = Co[a]	L = 5-methylpyrazole			
	M = Cd	M = Mn	M = Co	M = Ni
15.3	14.5 s[b]	14.2 s	14.1 s	14.0 s
11.8	11.2 vs	11.0 vs	10.95 vs	10.9 vs
10.8	10.1 s	10.0 s	9.95 s	9.9 s
5.65	5.39 w	5.31 w	5.28 w	5.24 w
5.00	4.73 w	4.70 w	4.65 w	4.62 w
4.82	4.56 m	4.54 m	4.49 m	4.47 m
3.93	3.70 s	3.68 s	3.64 m	3.63 s
3.12	2.96 m	2.94 m	2.92 w	2.90 m
2.81	2.65 m	2.63 m	2.62 w	2.60 m
2.59	2.45 m	2.43 m	2.41 m	2.40 m

[a] Crystal structure data: space group Pa3, a = 25.797 A. [b] vs = very strong, s = strong, m = medium, w = weak, vw = very weak.



obtained from X-ray powder diagrams. It was found that they are first of all mutually, structurally isomorphous, but secondly, the general line pattern of the diagrams was almost identical with the one observed for Co_4F_4(N-ethylimidazole)$_{12}(BF_4)_4$ [10]. Therefore, it is very likely that the compounds I–IV similarly will have tetrameric structures. In addition, this includes that obviously the molecular structure, especially the central M_4F_4 part of the molecule, remains quite unaffected by the change of ligand. Comparing the diagrams of the cobalt-5-MPZ and the cobalt-N-ethylimidazole compound, an increase in cell dimension is observed reflecting the difference in steric crowdiness (see Table II). Amongst the compounds I–IV an increase in cell dimension is found, following the sequence of increasing cationic radii (M = Ni < Co < Mn < Cd, see Table II).

In the compounds I–IV the 3(5)-MPZ ligand is expected to be coordinated having the methyl group in the 5-position. This way of coordination is sterically most favourable [14] and was observed in recently determined X-ray structures [12, 18]. An additional argument is found in the formation of dimeric, rather than tetrameric molecules for the compound CoF(3,5-dimethylpyrazole)$_3BF_4$, in which the ligand has an additional methyl group in the 3-position [7].

Although the arguments described above point strongly to a tetranuclear structure, they are not conclusive. Therefore, the structural proposal was checked by spectroscopic and magnetic measurements.

TABLE III. Far-IR Data (>180 cm^{-1}) for Compounds with Formula $M_4F_4(5\text{-MPZ})_{12}(BF_4)_4$.

M	Vibrations (cm^{-1})		
	Ligand	M–F stretching	M–N and other vibrations
Cd	352	316	237
Mn	356	322	260
Co	360	330	280
Ni	370	342	308 280 250

Spectroscopic and Magnetic Data

In the IR spectra of I–IV normal, unsplit, asymmetric B–F stretching and bending vibrations (ν_3 and ν_4) are observed, indicating that BF_4^- coordination takes not place. In the far-IR region (see Table III) besides the vibration bands of the M-(5-MPZ) group, one additional absorption is found at ~320 cm^{-1}, which is slightly dependent upon the metal.

In correspondence with earlier reports, this absorption is tentatively assigned to the metal–fluoride vibration [3, 5, 7, 8, 10]. The observed frequency is in agreement with the proposed tetrameric structure, as it falls in the same range as has been found earlier for six-coordinated metal atoms in similar tetranuclear compounds with formula $[M_4F_4(\text{N-RIz})_{12}](BF_4)_4$ (M = Mn, Cd or Co, N-RIz = N-ethyl- or N-propylimidazole) (300 cm^{-1}) [10]. In contrast, metal–fluoride vibrations in five-coordinated metal compounds show much higher frequencies, *e.g.* at ~445 cm^{-1} in $Co_2F_2L_6(BF_4)_2$ (L = 4-hydroxo-, 4-methyl-, 4-ethyl-, 4-propyl-, 4-benzyl-3,5-dimethylpyrazole [7]) and at ~420 cm^{-1} in $Co_2F_2L_6(BF_4)_2$ (L = lutidine-N-oxide [9]).

TABLE IV. UVV (Diffuse Reflectance) Data for Compounds with Formula $M_4F_4(5\text{-MPZ})_{12}(BF_4)_4$.

M	Maxima (kK)			
Co	20.4 (sh)	19.4	8.3	
Ni	25.6	15.5	13.7(sh)	9.0

The observed absorption bands in the UV–Vis spectra of III and IV (see Table IV) point to a slightly distorted octahedral surrounding of the metal atoms. The spectra and reported data correspond rather with six (B) than with five (A) coordinated metal atoms [19].

EPR spectra have been recorded for the compounds II–III as well as for the Mn-doped Cd compound I. Of the pure compounds only the Mn complex shows a resonance signal (isotropic, centered at g = 2.00 as expected for magnetically non-diluted Mn compounds). In the spectrum of the Mn-doped Cd compound, many lines occur. In addition to hyperfine splitting into six lines, originating from coupling of the unpaired electrons with the Mn nuclear spin ($I_{Mn} = 5/2$, $A_{Mn} = 91.5$ Gauss) also superhyperfine splitting into four lines is observed. This splitting is assigned to coupling with fluorine nuclear spins ($I_F = ½$). (Coupling with the nuclear spins of nitrogen ($I_N = 1$) would have resulted in at least seven lines (M/N ratio is 1/3). The observed A_F value of 16.6 Gauss corresponds to the one reported for MnF_6^{4-}: $A_F = 18.2$ Gauss [20]. The presence of four fluorine hyperfine lines in the spectrum indicates that every manganese atom is bound to three (magnetically equivalent) fluoride ions. This only agrees with a tetrameric structure, in which triple-bridging fluoride ions are present, thus supporting the conclusion drawn from the X-ray powder diagrams.

Temperature dependent magnetic susceptibility measurements (temperature range 2–80 K) have shown the existence of small interactions between the unpaired electrons on the metal atoms within the tetrameric structures of the cobalt and nickel compounds III and IV respectively. Maxima in the χ *vs.* T curves are found at 7.3 K (Co) and 9.0 K (Ni) (see also Table V). In contrast, the χ *vs.* T curve obtained for the manganese compound II shows no maximum. However, a sharp decrease is observed in the μ_{eff} value on lowering the temperature, as may be exemplified by the following results: T(μ_{eff} per Mn): 50.5 K (5.81); 40.1 K (5.37); 10.4 K (3.82); 5.4 K (3.17); 2.3 K (2.39). This effect is indicative of a small interaction between the unpaired electrons. The absence of a maximum in the χ *vs.* T curve is not fully unexpected, considering the results of the J/k calculations for the compounds $[M_4F_4(\text{N-ethylimidazole})_{12}](BF_4)_4$ (M = Co or Mn), which show an about tenfold smaller value for M = Mn with respect to Co [13] (see Table V).

TABLE V. Magnetic Susceptibility Data for Compounds of the Type $M_4F_4L_{12}(BF_4)_4$.[a]

M	L	T (χ_{max})	J/k
Mn	5-MPZ	<2 K	<2 K
Co	5-MPZ	7.3 K	
Ni	5-MPZ	9.0 K	
Mn	N-ethylimidazole	<2 K	–1.2 K[b]
Co	N-ethylimidazole	4.2 K	–10 K[b]

[a]Low temperature measurements (2–90 K). [b]See reference 13.

In view of the complexity of the investigated systems, exact J-values have not yet been calculated. Nevertheless, the present results show that the exchange interaction tends to be larger for the 5-MPZ than for the N-ethylimidazole compounds. Several magnetic investigations have shown that the bridging angle may be of great influence on the final J-value [21, 22]. Also for metal fluoride compounds a reduction of the J-value was observed, going from a 180° to a 90° superexchange pathway [13]. This may indicate that on replacing the N-ethylimidazole ligand in $M_4F_4(\text{N-ethylimidazole})_{12}(BF_4)_4$ compounds by 5-MPZ a small change in the M_4F_4 center takes place, resulting in slightly larger M–F–M angles.

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