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Synthesis, Structure, and Spectroscopic and Magnetic Properties of a New Class of Dimeric, Fluoro-Bridged High-Spin Cobalt(II) Compounds Containing Substituted-Pyrazole Ligands

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A new type of dimeric, five-coordinate, high-spin Co(II) compound, containing an asymmetric (CoF_2Co) bridge, is described. The product is formed upon reaction of cobalt(II) tetrafluoroborate with a 4-substituted 3,5-dimethylpyrazole in ethanol solution with triethyl orthoformate added for dehydration. The X-ray structure of one compound in the series, i.e., μ-difluoro-hexakis(3,5-dimethylpyrazole)dicobalt(II) bis(tetrafluoroborate), is described in detail. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 10.325 (5) Å, b = 13.753 (5) Å, c = 17.234 (6) Å, β = 117.92 (5)°, and Z = 4. Single-crystal X-ray diffraction data, complete to θ = 26° (Mo Kα radiation), were collected with a Nonius CAD-3 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is R_F = 5.6% for 3084 independent reflections. The symmetry around Co(II) is nearly trigonal bipyramidal. Ligand field spectra of the compounds can be interpreted on the basis of this symmetry. A unique type of hydrogen bonding is observed. This so-called trifurcated hydrogen bonding may cause the observed splitting of the (stretching) vibration at frequencies of the BF_4^- anion and the appearance of "forbidden" bands in the infrared spectra. In all compounds the magnetic-exchange coupling constant between the Co(II) ions is close to zero. The bridging Co–F–Co angle is 98.8 (2)°, in agreement with theories relating the Co–F–Co angle and magnetic exchange.

Introduction

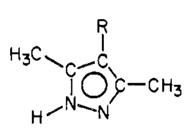
The BF_4^- anion is frequently used in coordination chemistry as a stabilizing counterion in cationic complexes. This ion is comparable in size with the perchlorate ion and has the advantage of not being a potential explosive. The anion is supposed to be stable in both aqueous and nonaqueous solution, although heating or strong bases may cause decomposition.

Recently, it has been shown that, in the presence of strong bases having bulky substituents (such as quinuclidine and 3,5-dimethylpyrazole), decomposition of the BF_4^- anion occurs, resulting in anhydrous metal fluorides for quinuclidine[1] and polymeric products of stoichiometry MF_2(ligand)$_2$ for 3,5-dimethylpyrazole.[2] In the case of 3-hydroxypyridine, a monomeric product MF_2(ligand)$_4$ has been analyzed, with trans fluoride anions.[3] Recently, a molybdenum fluoride coordination compound has been described.[4] Upon reaction of hydrated $Co(BF_4)_2$ with excess 3,5-dimethylpyrazole (and its 4-substituted products) under dehydrating conditions, compounds of empirical formula Co(ligand)$_3BF_5$ are obtained, which appeared to be low-molecular-weight products, with coordinated F^- ions, distorted BF_4^- anions, and Co(II) in a trigonal-bipyramidal geometry.

The present paper describes the spectroscopic and magnetic properties of this class of compounds. The molecular structure of one of these compounds is described in detail. Preliminary reports of this work have appeared.[5]

Experimental Section

Syntheses of the New Compounds. 4-Substituted 3,5-dimethylpyrazoles were prepared by condensation of acetylacetone (or its 3-substituted products) with hydrazine according to standard procedures.[6] In this way products of formula I with R = H (DMPZ),



I

Me (TMPZ), Et (EDMPZ), *n*-Pr (PDMPZ), and benzyl (BDMPZ) were obtained, which were purified by crystallization and characterized by NMR techniques. Cobalt(II) tetrafluoroborate was commercially available as the hydrate. Upon reaction of $Co(H_2O)_6(BF_4)_2$ with the pyrazole ligands in the ratio 1:4 using ethanol as a solvent and an excess of triethyl orthoformate as a dehydrating agent, violet crystals of composition Co(ligand)$_3BF_5$ separate.

With smaller amounts of the dehydrating agent or a lower ligand:metal ratio, pink products of formula Co(ligand)$_2F_2$ separate, as described previously.[2] Upon reaction of a 1:3 mixture of $Co(H_2O)_6(ClO_4)_2$ and $Co(H_2O)_6(BF_4)_2$ with DMPZ, a product of composition Co(DMPZ)$_3$F(ClO$_4$) can be isolated, which appears to be isomorphous with the corresponding BF_4 compound. The same product can also be prepared from equimolar amounts of Co(DMPZ)$_2F_2$ and Co(DMPZ)$_4$(ClO$_4$)$_2$ in $CHCl_3$.

Determination of the Molecular Structure. Violet crystals of CoF(DMPZ)$_3$(BF$_4$) were prepared as described above. The nearly octahedrally shaped crystal selected for X-ray analysis measured approximately 0.15 mm along the edges. Weissenberg photographs, taken with Cu Kα radiation, showed monoclinic diffraction symmetry and systematic extinctions of $P2_1/c$. The unit cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer (CAD-3), are a = 10.325 (5), b = 13.753 (5), c = 17.234 (6) Å, and β = 117.92 (5)° (Mo Kα_1 = 0.709 26 Å). The volume of the unit cell is 2162.58 Å^3 and contains four molecules.

The intensities were measured up to θ = 26° with the θ–2θ scan mode using Mo Kα radiation and a graphite monochromator (monochromator angle 6°). High intensities were reduced by nickel filters. From the 3084 reflections above background, 1664 were significantly (>2.85 $\sigma(I)$) different from the background intensity. In the reduction of the intensities to structure factors no correction for absorption has been applied ($\mu_{(Mo\ K\alpha)}$ = 9.7 cm^{-1}). Crystal data and experimental parameters are summarized in Table I.

The structure was solved by the heavy-atom method and refined by (blocked) full-matrix least-squares calculations using unit weights. The form factors used for Co, F, N, C, and B were obtained from Cromer and Mann[7] and those for H from Stewart et al.[8] In the last difference map a rest density was found, indicating a large thermal motion of the protons of the methyl groups. Therefore, these protons were not placed. Assigned isotropic temperature factors of the remaining hydrogen atoms were not refined. The final conventional

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Table I. Crystal Data and Experimental Parameters

		A. Crystal Data					
Formula	$CoF(DMPZ)_3(BF_4)$	c	17.234 (6) Å	Density (obsd)	1.4 g cm^{-3}		
Formula wt	453	β	117.92 (5)°	Density (calcd)	1.41 g cm^{-3}		
a	10.325 (5) Å	V	2162.6 Å^3	Space group	$P2_1/c$		
b	13.753 (5) Å	Z	4	μ(Mo Kα)	9.7 cm^{-1}		
		B. Experimental Parameters					
Radiation	λ(Mo Kα_1) 0.709 26 Å	Takeoff angle	4.4°	Data collected	3084		
Monochromator	Graphite	Max (sin θ)/λ	0.6180	Data with $I > 2.85\sigma(I)$	1664		

Table II. Final Parameters^a with Esd's in Parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	−53 (1)	268 (1)	856 (1)	546 (5)	366 (5)	509 (5)	−54 (4)	346 (4)	−28 (4)
F1$_{ax}$	762 (4)	772 (2)	−12 (2)	73 (2)	40 (2)	59 (2)	−12 (2)	45 (2)	−5 (2)
F2	−3477 (9)	−1185 (4)	4746 (5)	221 (8)	101 (4)	271 (8)	93 (5)	146 (7)	35 (5)
F3	−3425 (6)	−2778 (4)	4678 (3)	140 (5)	97 (4)	116 (4)	−33 (3)	65 (4)	−2 (3)
F4	−1432 (6)	−1999 (5)	5439 (3)	107 (4)	162 (5)	96 (4)	−6 (4)	19 (3)	−6 (4)
F5	−2455 (7)	−1905 (5)	4034 (3)	165 (6)	198 (6)	94 (4)	−36 (5)	81 (4)	2 (4)
B	−2747 (10)	−1917 (6)	4698 (5)	69 (5)	59 (5)	59 (5)	5 (4)	30 (4)	3 (4)
N1	−730 (6)	2355 (4)	371 (4)	58 (4)	49 (3)	92 (4)	−3 (3)	41 (4)	7 (3)
N11	−1308 (6)	1493 (3)	437 (3)	60 (3)	40 (3)	74 (3)	−7 (2)	43 (3)	4 (2)
N2	3047 (6)	879 (4)	1660 (3)	55 (3)	56 (3)	58 (3)	5 (3)	31 (3)	7 (3)
N21	2108 (6)	249 (4)	1748 (3)	61 (3)	54 (3)	65 (3)	7 (3)	37 (3)	12 (3)
N3	−1618 (6)	−1170 (4)	1415 (3)	72 (4)	47 (3)	54 (3)	−12 (3)	38 (3)	−3 (2)
N31	−948 (5)	−289 (4)	1596 (3)	63 (3)	49 (3)	52 (3)	−13 (3)	37 (3)	−7 (2)
C11	−2687 (7)	1693 (5)	228 (4)	52 (4)	58 (4)	71 (4)	−3 (3)	29 (4)	−2 (3)
C12	−2954 (8)	2684 (5)	42 (5)	61 (5)	60 (4)	92 (5)	12 (4)	31 (4)	2 (4)
C13	−1679 (8)	3091 (5)	135 (4)	64 (4)	46 (3)	72 (4)	5 (3)	25 (4)	2 (3)
C14	−1270 (9)	4107 (5)	17 (6)	96 (6)	38 (4)	120 (7)	−6 (4)	34 (5)	12 (4)
C15	−3753 (8)	901 (6)	163 (6)	58 (4)	84 (6)	132 (7)	−18 (4)	42 (5)	15 (5)
C21	2953 (9)	−202 (6)	2512 (5)	73 (5)	93 (6)	92 (5)	32 (5)	44 (5)	39 (5)
C22	4368 (9)	155 (8)	2862 (6)	63 (5)	132 (8)	87 (6)	33 (5)	29 (4)	40 (6)
C23	4411 (7)	843 (6)	2312 (5)	54 (4)	85 (5)	65 (4)	18 (4)	27 (4)	6 (4)
C24	5611 (8)	1489 (6)	2356 (5)	53 (4)	105 (6)	104 (6)	−10 (4)	32 (4)	1 (5)
C25	2364 (11)	−1011 (8)	2862 (7)	111 (8)	149 (9)	176 (10)	37 (7)	79 (7)	117 (8)
C31	−2167 (7)	−1394 (5)	1958 (4)	58 (4)	63 (4)	55 (4)	−3 (3)	32 (3)	12 (3)
C32	−1811 (8)	−624 (6)	2522 (4)	74 (5)	85 (5)	54 (4)	−12 (4)	43 (4)	−2 (4)
C33	−1063 (7)	45 (5)	2285 (4)	63 (4)	66 (4)	51 (3)	−11 (3)	35 (3)	−9 (3)
C34	−446 (9)	1034 (6)	2667 (5)	110 (6)	83 (5)	84 (5)	−41 (5)	61 (5)	−45 (4)
C35	−2979 (6)	−2327 (5)	1878 (5)	90 (5)	66 (4)	93 (5)	−21 (4)	53 (5)	15 (4)

Atom	x/a	y/b	z/c	U, Å^2	Atom	x/a	y/b	z/c	U, Å^2
H11	3 (7)	242 (5)	−46 (4)	63	H28	507 (9)	−3 (6)	332 (5)	114
H18	−387 (7)	305 (5)	−12 (4)	76	H31	−174 (7)	−146 (5)	101 (4)	63
H21	282 (8)	114 (5)	126 (4)	63	H38	−202 (7)	−63 (5)	295 (4)	76

^{a} The fractional atomic coordinates are $\times 10^4$ for the nonhydrogen atoms and $\times 10^3$ for the hydrogen atoms with the anisotropic thermal parameters for Co given in Å^2 $\times$ 10^4 and the other atoms in Å^2 $\times$ 10^3. The U_{ij} coefficients are given by the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

R index ($\sum||F_o| - |F_c||/\sum|F_o| \times 100$) is 5.6%. All calculations were performed on an IBM 370/158 computer, using the computer programs from XRAY 72.[9] The final set of atomic and thermal parameters is given in Table II. A table of observed and calculated structure factors is available.[10]

Spectral and Magnetic Measurements. Infrared and far-infrared spectra were obtained on Hilger and Watts (4000–650 cm^{-1}), Beckman Acculab 6 (4000–250 cm^{-1}), Perkin-Elmer 521 (700–250 cm^{-1}), and Beckman IR 720 (500–100 cm^{-1}) instruments. Samples were recorded either as Nujol mulls between NaCl or KBr plates (4000–400 cm^{-1}) or as pressed polythene disks (500–100 cm^{-1}). Ligand field spectra were recorded on a Beckman DK-2 instrument (30 000–4000 cm^{-1}) by the diffuse-reflectance technique and in CH_2Cl_2 solution.

Room-temperature magnetic susceptibility measurements were obtained by the NMR method in solution.[11] Proton and fluorine NMR spectra were performed on standard Varian T60 and XL100 instruments. Low-temperature susceptibilities were performed on a PAR vibrating-sample magnetometer in the 4–100 K region as described elsewhere.[12]

Results and Discussion

General Data. Analytical data, melting point, and conductivity data of the new compounds are summarized in Table III. Ligand field spectra and magnetic data are listed in Table IV, together with a Co–F vibration. According to the empirical formula of the compounds, the BF_4^- anion must have reacted with the solvent or the ligand, delivering F^- ions. Such a decomposition is unusual and has been observed previously in a few cases. Musgrave and Lin[1] observed products BF_3(ligand), with ligand = quinuclidine, Guichelaar observed linear-chain systems MF_2(ligand)$_2$ for 3,5-dimethylpyrazole,[2] Smit[3] found tetragonal species MF_2(ligand)$_4$ in case of 3-hydroxypyridine, whereas very recently Hidai and co-workers found a species $[Mo(F)(N_2H_2)(dppe)_2](BF_4)$. The new products were analyzed by standard spectroscopic and magnetic techniques; the results will be described below.

Conductivity measurements in methylene chloride showed that the compounds are hardly dissociated in solution (Table III), indicating either coordinated BF_4^- ions or strong cation–anion pairing. The compounds are readily soluble in weakly polar solvents, whereas the compound with R = Et dissolves even in benzene and CCl_4.

Description of the Molecular Structure of $(Co(DMPZ)_3F)_2(BF_4)_2$. Figure 1 provides an illustration of the crystallographic independent half of the dimeric molecule. A part of the second half of the molecule, generated by the inversion center, is also shown in Figure 1 to illustrate the interaction between cation and anion. Bond distances and angles are given in Table V.

Two Co atoms and two F atoms are involved in a strictly

Table III. Analytical Data, Melting Points, and Conductivity in CH_2Cl_2 for Dimeric Fluoro-Bridged Co(II) Compounds

	% Co		% C		% H		% N		% B		% F			
Compd	Calcd	Fnd	Calcd	Fnd	Calcd	Fnd	Calcd	Fnd	Calcd	Fnd	Calcd	Fnd	Mp,[b] °C	Conduct in CH_2Cl_2
$Co_2(DMPZ)_6F_2(BF_4)_2$	13.02	13.18	39.76	40.18	5.30	5.51	18.55	18.45	2.39	1.91	20.98	19.95	221	7.4[a]
$Co_2(TMPZ)_6F_2(BF_4)_2$	11.91	12.21	43.66	44.04	6.06	5.78	16.98	16.39	2.18	2.04	19.20	18.48	215	8.4
$Co_2(EDMPZ)_6F_2(BF_4)_2$	10.98	11.18	47.0	47.0	6.7	6.8	15.65	15.92	2.01	1.82	17.70	16.72	201	8.1
$Co_2(PDMPZ)_6F_2(BF_4)_2$	10.18	10.85	49.8	49.2	7.3	7.6	14.51	14.66	1.87	1.81	16.42	15.11	142	2.8
$Co_2(BDMPZ)_6F_2(BF_4)_2$	8.15	8.43	59.8	59.6	5.8	6.0	11.62	11.57	1.49	1.35	13.14	12.37	229	6.8
$Co_2(DMPZ)_6F_2(ClO_4)_2$	12.66	12.80	38.60	38.99	5.16	5.44	18.05	18.38	0		4.08	7.25		

[a] Measured as 10^{-3} M solutions; conductivity expressed in $cm^2\ \Omega^{-1}\ mol^{-1}$. [b] Melting with decomposition.

Table IV. Ligand Field Spectra, Far-IR Co–F Stretch, and Solution Magnetic Moments at Room Temperature of Dimeric Fluoro-Bridged Co(II) Compounds

Compd	Co–F str, cm^{-1}	Ligand field max, $cm^{-1} \times 10^3$	Magnetic moment in CH_2Cl_2, μ_B
$Co_2(DMPZ)_6F_2(BF_4)_2$	458	20.0 sh 17.9 12.2 5.5	4.5
$Co_2(TMPZ)_6F_2(BF_4)_2$	440	20.0 sh 18.0 11.6 5.5	4.5
$Co_2(EDMPZ)_6F_2(BF_4)_2$	445	20.0 sh 17.8 11.8[a] 5.4	4.6
$Co_2(PDMPZ)_6F_2(BF_4)_2$	446	20.0 sh 18.2 11.8 5.4	
$Co_2(BDMPZ)_6F_2(BF_4)_2$	447	20.0 sh 17.5 12.0 5.4	4.6
$Co_2(DMPZ)_6F_2(ClO_4)_2$	460	20.0 sh 17.9 12.2 5.5	

[a] A small splitting is observed.

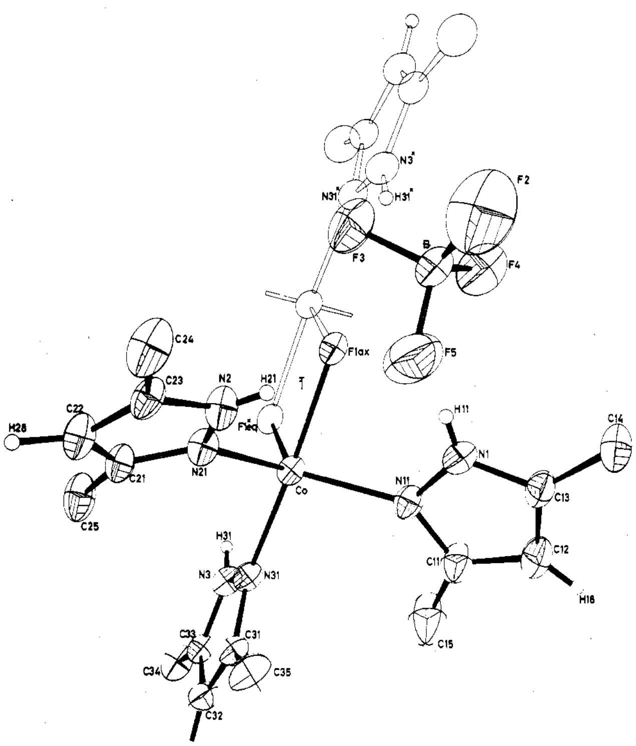

Figure 1. ORTEP drawing of the asymmetric part of $Co_2F_2(DMPZ)_6(BF_4)_2$; 20% probability ellipsoids are used.

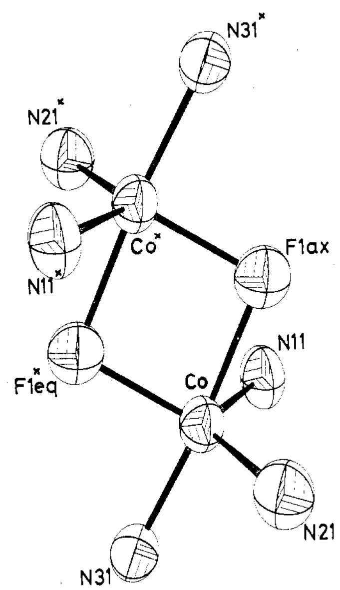

Figure 2. ORTEP drawing of the geometry around cobalt in the dimer.

planar bridging system. The Co–Co distance is 3.092 (2) Å. The bridging Co–F–Co angle is 98.8 (2)°. The maximum deviation from perfect trigonal-bipyramidal geometry at the Co centers is 8°. One F atom and two ring ligands are in the equatorial plane and the F atom of the bridge, together with the third ligand, are in the axial direction. The equatorial Co–F bond length differs significantly from the axial Co–F bond length: 1.924 (4) and 2.146 (4) Å, respectively. The Co–N bond lengths of 2.033 (5), 2.040 (5), and 2.042 (6) Å are intermediate between those found for tetrahedral and octahedral Co(II) azole compounds.[13] The geometry of the bridge and of the coordination around Co is shown in Figure 2. The two BF_4 groups interact with the dimer via hydrogen contacts. Each N hydrogen atom of a pyrazole ring has one contact with an axial F atom and two contacts with two F atoms of a BF_4 group. The geometry of the interion contacts is depicted in Figure 3. The N–H···F distances are, in most cases, shorter than the accepted van der Waals distance of 2.65 Å. So it looks like the rings accept a rotational position around the Co–N bonds as to minimize all N–H···F contacts. This hydrogen bonding system is an example of the rarely observed trifurcated hydrogen bond.[14] The divergence in the different bonds is smaller than found in a recent study,[14] where H···Cl contacts between 2.38 and 3.29 Å and N···Cl contacts between 3.29 and 3.67 Å were observed. The symmetry of the BF_4^- anion is distorted tetrahedral, with the B–F bond not involved in hydrogen bonding being the smallest.

The structure shows an example of a distorted BF_4^- ion not caused by coordination to a metal ion but by its unique hydrogen bonding.

Spectroscopic Measurements. Infrared spectra of the compounds show the usual pattern of a coordination compound containing a coordinated organic molecule and a counterion.

The vibrations of the BF_4^- ion (and also those of the ClO_4^- ion in the corresponding perchlorate) show a distinct splitting of the degenerate asymmetric vibrations and an appearance of the "forbidden" symmetrical stretching vibration. This

Table V. Bond Distances and Angles in $[Co_2(DMPZ)_6F_2](BF_4)_2$

Bond Distances, Å

Coordination of Co and B		Five-membered rings: Ring I		Ring II		Ring III	
Co-N11	2.040 (5)	N11-C11	1.324 (9)	N21-C21	1.344 (9)	N31-C31	1.330 (9)
Co-N21	2.033 (5)	C11-C12	1.398 (10)	C21-C22	1.384 (12)	C31-C32	1.380 (11)
Co-N31	2.042 (6)	C12-C13	1.369 (12)	C22-C23	1.355 (13)	C32-C33	1.366 (10)
Co-F1$_{eq}^{a}$	1.924 (3)	C13-N1	1.333 (9)	C23-N2	1.329 (7)	C33-N3	1.337 (11)
Co-F1$_{ax}$	2.146 (4)	N1-N11	1.356 (8)	N2-N21	1.361 (9)	N3-N31	1.357 (7)
B-F2	1.285 (12)	C11-C15	1.514 (11)	C21-C25	1.521 (16)	C31-C35	1.516 (10)
B-F3	1.368 (11)	C13-C14	1.501 (10)	C23-C24	1.497 (12)	C33-C34	1.504 (10)
B-F4	1.365 (8)	C12-H18	0.99 (7)	C22-H28	0.82 (7)	C32-H38	0.86 (8)
B-F5	1.313 (13)	N1-H11	0.73 (7)	N2-H21	0.72 (7)	N3-H31	0.76 (7)

Bond Angles, Deg

Coordination of Co and B		Five-membered rings: Ring I		Ring II		Ring III	
N11-Co-N21	124.6 (2)	Co-N11-C11	133.7 (5)	Co-N21-C21	136.6 (6)	Co-N31-C31	133.2 (4)
N11-Co-N31	97.6 (2)	Co-N11-N1	121.3 (4)	Co-N21-N2	119.6 (4)	Co-N31-N3	121.5 (4)
N11-Co-F1$_{eq}^{a}$	113.1 (2)	N11-C11-C15	121.6 (6)	N21-C21-C25	122.0 (7)	N31-C31-C35	120.2 (7)
N11-Co-F1$_{ax}$	83.0 (2)	N11-C11-C12	109.6 (7)	N21-C21-C22	109.4 (8)	N31-C31-C32	109.3 (6)
N21-Co-N31	100.4 (2)	C11-N11-N1	104.8 (5)	C21-N21-N2	103.6 (5)	C31-N31-N3	105.3 (6)
N21-Co-F1$_{eq}^{a}$	117.2 (2)	C12-C11-C25	128.7 (7)	C22-C21-C25	128.6 (7)	C32-C31-C35	130.5 (7)
N21-Co-F1$_{ax}$	83.2 (2)	C11-C12-H18	128.0 (4)	C21-C22-H28	126.0 (7)	C31-C32-H38	132.0 (4)
N31-Co-F1$_{eq}^{a}$	94.0 (2)	C13-C12-H18	125.0 (4)	C23-C22-H28	126.0 (7)	C33-C32-H38	120.0 (4)
N31-Co-F1$_{ax}$	175.0 (2)	C12-C13-C14	132.9 (7)	C22-C23-C24	132.6 (6)	C32-C33-C34	132.7 (8)
F1$_{eq}^{a}$-Co-F1$_{ax}$	81.2 (2)	C12-C13-N1	104.8 (6)	C22-C23-N2	104.4 (7)	C32-C33-N3	105.0 (6)
F2-B-F3	111.7 (9)	N1-C13-C14	122.3 (7)	N2-C23-C24	123.0 (7)	N3-C33-C34	122.2 (6)
F2-B-F4	111.1 (7)	C13-N1-H11	122.0 (5)	C23-N2-H21	125.0 (6)	C33-N3-H31	125.0 (6)
F2-B-F5	115.3 (8)	C13-N1-N11	113.5 (6)	C23-N2-N21	114.2 (6)	C33-N3-N31	112.5 (6)
F3-B-F4	103.0 (6)	N11-N1-H11	125.0 (5)	N21-N2-H21	120.0 (6)	N31-N3-H31	122.0 (6)
F3-B-F5	108.2 (7)						
F4-B-F5	106.7 (8)						

[a] Atom generated by center of symmetry.

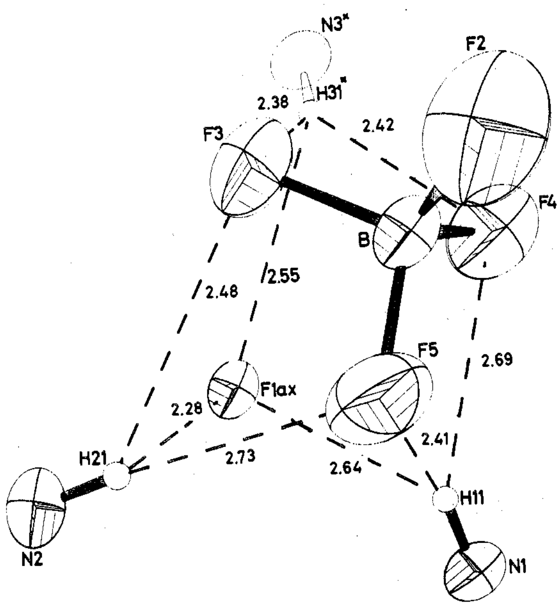

Figure 3. Interaction of the BF_4^- anion with the N–H groups of the $[Co_2F_2(DMPZ)_6]^{2+}$ cation. H–F distances are given in the figure. N–F distances vary between 2.74 and 3.26 Å. Angles N–H–F vary between 105 and 163°.

phenomenon is well-known in the literature and is usually ascribed to coordination of the anion.

As shown by the crystal-structure determination, the present phenomenon is due to the unusual type of hydrogen bonding. Therefore, one should be aware of the fact that splitting of the degenerate B–F stretching vibration and the appearance of the forbidden bands in the infrared do not necessarily imply coordination of the BF_4 group.

Far-infrared spectra show a strong band around 450 cm^{-1}, assigned to a Co–F stretching vibration. Below 350 cm^{-1} several bands are observed that cannot be assigned unambiguously but must be due to Co–N and Co–F vibrations.

Ligand field spectra of the compounds are almost identical for the several ligands (Table IV) and hardly change upon going to the solute state. This indicates that the same species is present in the solid state and in solution of $CHCl_3$ and CH_2Cl_2. The strong interaction between the BF_4^- ions and the N–H groups seems to be present in solution as well, as deduced from the conductivity data listed in Table III. The shape of the absorption bands and the positions agree with a trigonal-bipyramidal coordination geometry for high-spin Co(II).[15] Addition of extra ligands to this solution does not change the ligand field spectrum, indicating that a single Co(II) species must be present. Proton NMR spectra of the compounds dissolved in CH_2Cl_2 revealed the magnetic moments of the compounds that are listed in Table IV. The observed paramagnetic shifts in the proton resonances are well-known and agree with high-spin Co(II). Upon addition of extra ligand molecules, the paramagnetic shifts decrease, which is indicative for a fast ligand exchange with respect to the NMR time scale. Cooling of the solution did not yield separate signals for free and coordinated ligands (down to 210 K).

The magnetic behavior in the solid state and the interpretation of the low-temperature magnetic data are described below.

To obtain more information about the ion pairing, ^{19}F NMR spectra of a few solutions were recorded. It appeared that only resonances attributed to BF_4^- were observed. Signals due to F^- ions were not observed, probably due to a too large shift and a too large paramagnetic line broadening.

Even the signal of the BF_4^- ion appeared to be shifted with respect to a free BF_4^- ion such as in Bu_4NBF_4. This shift must

Table VI. Magnetic Data and ν(Co–F) of Several Dimeric Co(II) Compounds (Uncertainties in the Last Digits are in Parentheses)

Compd	μ(4.2 K)	μ(10 K)	μ(120 K)	μ(310 K)[a]	ν(Co–F), cm^{-1}
$Co_2(BDMPZ)_6F_2(BF_4)_2$	4.32 (4)	4.6 (1)	*b*	4.6 (2)	447
$Co_2(DMPZ)_6F_2(BF_4)_2$	4.20 (4)	4.4 (1)	4.6 (1)	4.5 (2)	458
$Co_2(EDMPZ)_6F_2(BF_4)_2$	3.51 (4)	3.9 (1)	4.5 (1)	4.6 (2)	445
$Co_2(TMPZ)_6F_2(BF_4)_2$	2.11 (3)	2.9 (1)	4.3 (1)	4.5 (2)	440

[a] NMR method (Table IV). μ values are in μ_B. [b] Not investigated.

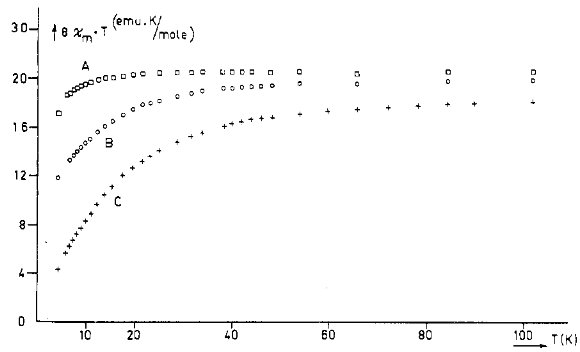

Figure 4. Values of μ^2_{eff} as a function of temperature for three dimeric Co(II) compounds: A, $Co_2(DMPZ)_6F_2(BF_4)_2$; B, $Co_2(EDMPZ)_6F_2(BF_4)_2$; C, $Co_2(TMPZ)_6F_2(BF_4)_2$.

be due to the unusual interaction between the cation and the anion. After addition of extra BF_4^- ions, a single signal shifted in the direction of free BF_4^- is observed, indicative of fast exchange between BF_4^- and ion-paired BF_4^-. This cation–anion pairing must be responsible for the good solubility and high stability of the dimeric species in a weakly polar solvent.

Magnetic Interaction. The dimeric species CoF_2Co is unusual among transition-metal complexes. In fact, only Cp_2TiF has been suggested to be dimeric in nature with fluoro bridges, although the structure has not yet been proven crystallographically.[16] To study the nature of the magnetic interaction between the Co(II) ions, magnetic susceptibility measurements of a few compounds were determined down to 4 K. The results of these measurements are listed in Table VI. A graphical representation is given in Figure 4. The accurate magnitude of the magnetic exchange coupling constant is hard to determine from these data alone. More accurate data down to 2 K and saturation studies in strong magnetic field are needed for detailed information between structural and magnetic data.[17] Nevertheless, from the table and the figure it is clear that a small but distinct interaction occurs between the metal ions. The magnitude of the interaction varies from compound to compound. The bridge geometry actually determines sign and magnitude of the exchange.[18] It seems likely that a particular ligand influences the molecular structure and probably the bridge symmetry to such an extent that different Co–F–Co angles and Co–F distances result. It is known that the Co–F–Co angles close to 100° result in a small magnetic exchange.[19,20]

Additional information about the variation of Co–F distances and Co–F–Co angles in the different compounds may come from far-IR spectra, since it is well-known that metal–ligand vibrations vary as a function of bonding distances and angles.[21]

To investigate a possible relationship between the magnitude of the exchange and far-IR data, the value of the highest Co–F stretching frequency (near 450 cm^{-1}) has also been listed in Table VI. It appears that at least for the alkyl substituted compounds the largest exchange (in case of TMPZ) corresponds with the smallest Co–F stretch, whereas the smallest exchange (in case of DMPZ) corresponds with the highest Co–F stretch.

To find out whether or not different substituents yield different Co–F distances and Co–F–Co angles, and to see to what extent these are related to differences in far-IR spectra and magnetic exchange, more structural data are needed. This is left for future investigation. Table VI finally shows that the NMR room-temperature susceptibility data are in fair agreement with the low-temperature solid-state data. The small differences are due to the fact that at low temperatures different electronic levels become occupied due to depopulation of the upper $S = {}^3/_2$ levels.

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Registry No. $Co_2(DMPZ)_6F_2(BF_4)_2$, 60308-08-9; $Co_2(TMPZ)_6F_2(BF_4)_2$, 61003-06-3; $Co_2(EDMPZ)_6F_6(BF_4)_2$, 61003-24-5; $Co_2(PDMPZ)_6F_2(BF_4)_2$, 61003-26-7; $Co_2(BDMPZ)_6F_2(BF_4)_2$, 61003-28-9; $Co_2(DMPZ)_6F_2(ClO_4)_2$, 66538-06-5.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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