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Binuclear Metal Complexes: Heterobinuclear Complexes with a Schiff Base derived from *o*-Acetoacetylphenol and Ethylenediamine

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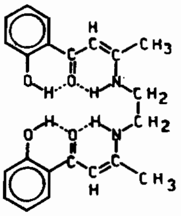
A series of heterobinuclear complexes, prepared from a binucleating ligand containing two different coordinating sites are reported. The ligand is a Schiff base derived from the reaction of o-acetoacetylphenol and ethylenediamine (H_4aapen). The mononuclear Cu(H_2aapen) and Ni(H_2aapen) chelates have been used as ligands to prepare the heterobinuclear compounds of the type NiM'(aapen) and CuM'(aapen) (M' = Cu(II), Co(II), Ni(II), Mn(II), NiFe(aapen)Cl and CuFe(aapen)Cl·H_2O. The characterization of these binuclear complexes has been carried out by analytical, infrared, electronic and magnetic susceptibility data. No intramolecular exchange of metal ions in the coordination positions occurred in the process of the preparation.

Introduction

In the latest decade it has been increasingly recognized that molecules containing multiple metal centers are potentially important in catalytic processes. Accordingly, many attempts have been undertaken to elucidate the nature of the metal–metal interaction. One obvious reflection of this attitude can be found in the rapid development of the metal cluster chemistry. Another approach to this may be to design multidentate ligands which are capable of coordinating two metal ions in proximity. The study of the properties and the characteristics of these binuclear complexes might clarify, perhaps even mimic, the behaviour of the more sophisticated multimetallic systems.

Earlier reports in this series [1–10] have described heterobinuclear complexes derived from binucleating Schiff base ligands. In the previous papers the Cu(II)–M(II) and Ni(II)–M(II) heterobinuclear complexes have been obtained using the Schiff base H_4fsadiam formed from 3-formylsalicylic acid and diamine in the molar ratio 1:2 (diam = 1,2-diaminoethane [1, 8, 11], 1,3-diaminopropane [8], 2,3-diaminobutane, 1,2-diaminocyclohexane and *o*-phenylenediamine [7, 10]). Other types of ligands were the Schiff bases derived from 2,4,6-heptanetrione [13] and *o*-acetoacetylphenol [12].

In this paper we report the synthesis and characterization of heterobinuclear complexes derived from the ligand:



H_4 aapen

By reacting the mononuclear complexes Cu(H_2aapen) and Ni(H_2aapen) [5] with the appropriate metal salts, heterobinuclear compounds have been prepared, which are represented by MM'(aapen), where M is an inside metal ion coordinated by the O_2N_2 donor set and M' is an outside metal ion coordinated by the O_2O_2 donor set.

Experimental

Syntheses

o-Acetoacetylphenol was prepared by the method of Wittig [14]. The ligand H_4aapen and the mononuclear complexes Cu(H_2aapen) and Ni(H_2aapen) have been prepared according to the literature [5].

Cu_2(aapen)

To the mononuclear complex Cu(H_2aapen) (0.001 mol) dissolved in pyridine (30 ml) was added lithium hydroxide (0.002 mol) in ethanol. The solution was

TABLE I. Elemental Analyses of the Complexes.

	C %		N %		H %		Cu %		Others %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Cu_2(aapen)	52.46	52.16	5.59	5.46	4.00	4.14	25.24	24.91		
CuCo(aapen)	52.95	52.70	5.64	5.63	4.04	4.26	12.73	12.54		
CuFe(aapen)Cl·H_2O	48.10	47.82	5.12	5.47	4.03	3.95	11.56	11.41	10.16	9.76 (Fe)
CuMn(aapen)·$2H_2O$	49.75	49.74	5.30	5.25	4.54	4.19	11.96	11.48	10.34	10.35 (Mn)
Ni_2(aapen)	53.50	53.34	5.70	5.86	4.05	4.17				
NiCu(aapen)	52.96	53.18	5.64	5.42	4.04	4.22	12.74	12.01		
NiCo(aapen)	53.46	52.91	5.69	5.69	4.07	4.33				
NiFe(aapen)Cl	50.2	50.8	5.34	5.26	3.82	3.93			6.73 10.6	6.21 (Cl) 10.01 (Fe)
NiMn(aapen)·$2H_2O$	50.22	50.63	5.35	5.21	4.56	4.04			10.44	10.01 (Mn)

kept at 60–70 °C for 15 min and an ethanolic solution (15 ml) of copper(II) acetate dihydrate (0.001 mol) was added. The solution turned from dark green to brown. The heating and stirring was continued for about 4 hr. The pyridine in the solution was removed at reduced pressure and the residue was treated with hot ethanol. The hot solution was filtered and the solid residue was washed with ethanol and dried under reduced pressure over silica gel.

The complexes CuMn(aapen), NiMn(aapen), Ni_2(aapen) and Cu_2(aapen) were prepared by similar methods.

MFe(aapen)Cl·nH$_2$O (M = Cu, n = 1; M = Ni, n = 0)

To hot a pyridine solution prepared from mononuclear M(H_2aapen), lithium hydroxide and lithium chloride (five-fold excess), an ethanolic solution of anhydrous iron(III) chloride was added to give a brown solution. The reaction mixture was maintained at 60–70 °C under stirring for about 4 hr. The solvent was removed under reduced pressure and the residue was treated with hot degassed ethanol. The hot solution was filtered and the solid residue was washed with ethanol and dried under reduced pressure over silica gel. All the operations were carried out under nitrogen atmosphere.

MCo(aapen) (M = Cu(II) and Ni(II))

The synthetic method for these complexes is nearly the same as that for Cu_2(aapen), but the reaction was carried out under nitrogen atmosphere.

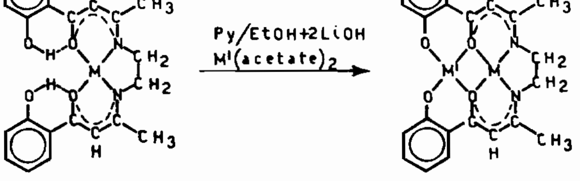
Measurements

Carbon, hydrogen and nitrogen analyses were carried out at the Center of Elemental Analysis of Padua University (Table I). The metal analyses were carried out with a Perkin-Elmer 403 model spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 577 model spectrophotometer using KBr discs. Electronic spectra were measured with a Shimadzu Multipurpose MSP 5000 model spectrophotometer by reflection on a powder sample. Magnetic susceptibilities were determined by the Faraday method from the liquid nitrogen temperature to room temperature, the apparatus being calibrated with $HgCo(NCS)_4$ [15]. Diamagnetic corrections were carried out using Pascal's constants [16].

Results and Discussion

The ligand H_4aapen has one site with two nitrogen and two oxygen atoms (N_2O_2) and a second site with four oxygen atoms (O_2O_2), the two central oxygens being common in both sites.

Once it was established that in the two mononuclear Cu(H_2aapen) and Ni(H_2aapen) complexes the metal ions occupy the N_2O_2 site, it should become feasible to prepare pure mixed metal chelates, in which the position of the two metal ions are in predicated environments. The binuclear complexes were prepared according to the reaction:



Although our synthetic method for heterobinuclear complexes was similar to those already reported [5, 11, 12], we could not always obtain pure compounds. We should be aware that some binuclear complexes were occasionally contaminated with monomeric or homobinuclear species and also

TABLE II. Selected IR Bands (cm^{-1}) and Effective Magnetic Moments (BM) of the Complexes.

	$\nu_{C\cdots O}$ + $C\cdots C$	$\nu_{C\cdots N}$	Phenolic $\nu_{C–O}$	μ_{eff} (T°)
Cu_2(aapen)	1600 (br)	1515	1320	0.64 (297.3)
CuCo(aapen)	1598	1512	1310 w	4.57 (294.2)
CuFe(aapen)Cl•H_2O	1603	1518	1310 sh	6.13 (295.4)
CuMn(aapen)•$2H_2O$	1600	1522	–	3.80 (295.4)
Ni_2(aapen)	1595, 1580 sh	1515	1310 sh	2.89 (296.6)
NiCu(aapen)	1600 br	1518	1315	2.27 (295.9)
NiCo(aapen)	1595, 1590 sh	1510	1320 sh	4.55 (295.4)
NiFe(aapen)Cl	1598	1515	1310 hs	5.96 (296.4)
NiMn(aapen)•$2H_2O$	1595	1522	–	4.12 (297.6)

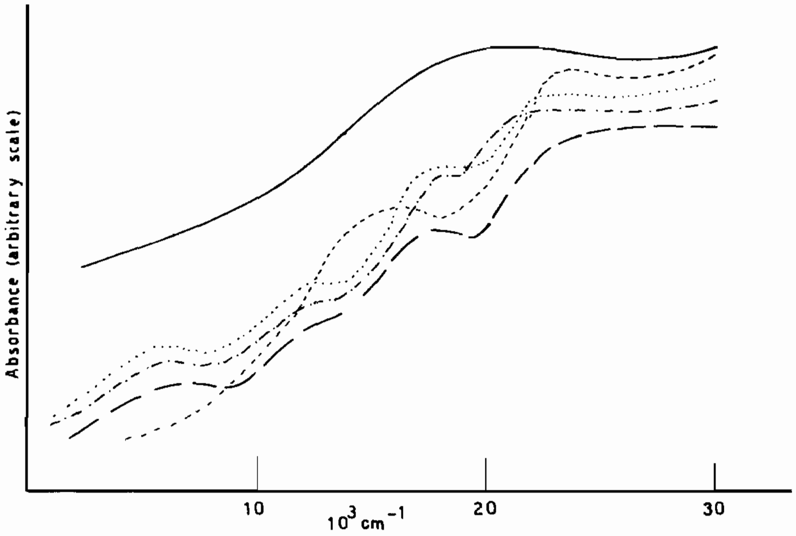


Fig. 1. Electronic spectra of (———) CuFe(aapen)Cl•H_2O, (------) CuCo(aapen), (-·······-) Cu_2(aapen) and (·······) CuMn(aapen)•$2H_2O$.

impurity due to a different oxidation state of the second metal might be present. The synthesis of CuNi(aapen) complex was unsuccessful, the main product being Li_2Cu(aapen) and some amount of Cu_2(aapen). By the reaction of Cu(H_2aapen) with $FeCl_2$ under our reaction condition, we have obtained a mixture of two different complexes. The elemental analyses gave values which fit well with the value calculated for a mixture of CuFe(aapen) and Fe_2(aapen) in molar ratio 1:1. It was impossible to separate the two complexes from the mixture owing the very similar solubilities in the common organic solvents.

Moreover, by the reaction of M(H_2aapen) complexes with $MnCl_2$ in the open atmosphere we have prepared the binuclear complexes formulated as MMn(aapen)•$2H_2O$ on the grounds of the elemental analyses. However magnetic susceptibilities do not follow any law on varying the temperature in the 70–300 K range (magnetic moments at room temperature are 3.80 μ_B for CuMn(aapen)•$2H_2O$ and 4.12 μ_B for NiMn(aapen)•$2H_2O$). We suppose that products of the aerobic oxidation of Mn(II) may be present; recently three types of oxidation products including Mn(III) and Mn(IV) have been obtained from pyridine solutions of Mn(II) complexes [22]. General features of the IR spectra of the binuclear chelates are very similar to each other but different from those of the mononuclear parent compounds. Although the molecules are too complex to consider the assignment of each band, it seems that the band at 1600 cm^{-1} may be assigned to C–O or C=C + C–O stretching modes, the band at 1500 cm^{-1} is due to the C–N stretching vibration and the band in the 1290–1320 cm^{-1} region is due to the C–O (phenolic stretch (Table II)).

Because of the low solubility of the complexes in most solvents, the electronic spectra were measured

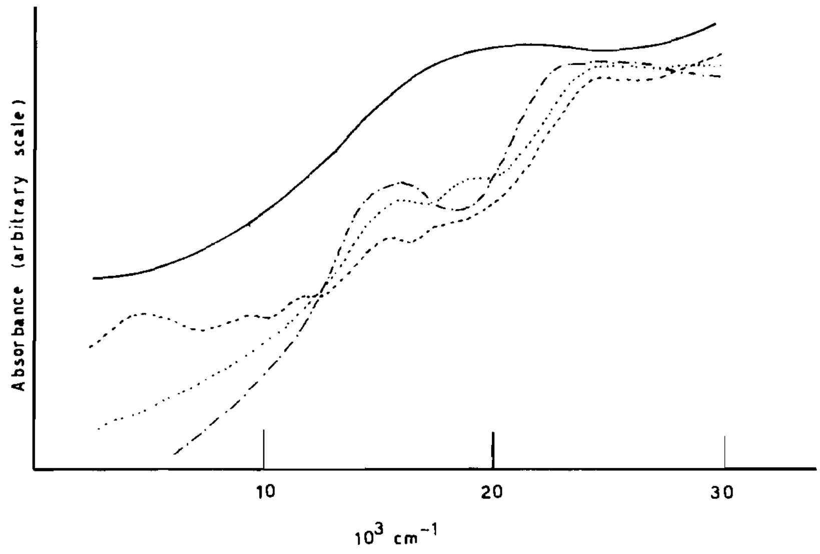


Fig. 2. Electronic spectra of (———) NiFe(aapen)Cl, (-------) NiCu(aapen), (········) Ni_2(aapen), (-·-·-·-·-) NiMn(aapen)·$2H_2O$ and (– – – –) NiCo(aapen).

by reflectance on powdered sample; they are given in Fig. 1 and Fig. 2.

The reflectance spectrum of Cu_2(aapen) shows a broad band centered at 15,100 cm^{-1} and suggests that both copper(II) ions have a nearly planar coordination.

The room temperature magnetic moment is lower than the spin only value expected for a d^9 system and suggests a partial spin pairing between the copper(II) ions. Its susceptibility, measured over a temperature range 77–300 K, can be interpreted on the basis of the Bleany–Bowers equation [17]:

$$\chi_A = \frac{Ng^2\beta^2}{3KT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha$$

in which each symbol has the usual meaning. Since Cu_2(aapen) is likely to contain some extent of mononuclear species, we could fit the experimental curve to the theoretical one by substituting $(\chi_A - \chi'_A)$ for χ_A or assuming that 8.5% of Cu(H_2aapen) is present (Table III). From the best fit $-2J$, g and $N\alpha$ were evaluated to be 730 cm^{-1}, 2.16 and 60 × 10^{-6} esu/mol respectively. This large value of $-2J$ indicates a very strong antiferromagnetic exchange interaction between the copper(II) atoms, which may be observed for a planar ring system $\mathrm{Cu}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Cu}$ [18]. On the other hand much weaker coupling has been observed in a bent four-membered ring [19]. The planarity of $\mathrm{Cu}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Cu}$ ring in our complex has been confirmed by an X-ray investigation on single crystal obtained from dmso [20]. The crystal consists of a binuclear Cu_2(aapen)·H_2O molecule as illustrated in Fig. 3; one copper(II) is four coordinated in the inner donor atom set N_2O_2, while the other is five coordinated in a square pyramidal geometry with a water molecule in the apical position. The $\mathrm{Cu}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Cu}$ ring has a dihedral angle of about 6°.

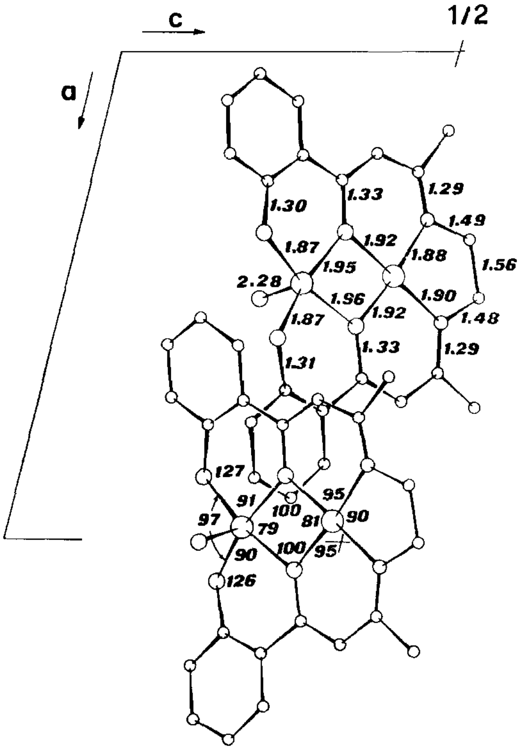


Fig. 3. Projection of the structure of Cu_2(aapen)·H_2O down the *b* axis. The main bond distances (Å) and angles (°) are reported.

TABLE III. Temperature Dependence of the Magnetic Moments.

Cu_2(aapen)

T(K)	82.2	102.0	121.6	131.2	150.5	170.2	199.9	219.6	239.0	258.9	278.3	297.3
$\chi_A \times 10^6$	503	431	351	342	318	301	301	309	318	331	344	359
$\chi'_A \times 10^6$ [a]	53	69	47	60	72	84	116	141	163	188	211	235

Theoretical ($-2J = -730$ cm^{-1}, $g = 2.16$, $N\alpha = 60 \times 10^{-6}$)

T(K)	80	100	125	150	175	200	220	240	260	280	300	
$\chi_A \times 10^6$	60	61	63	72	87	110	132	157	184	211	238	

CuCo(aapen)

T(K)	82.2	93.0	112.3	131.6	151.3	170.6	190.3	209.1	228.4	247.5	271.7	294.2
$\chi_M \times 10^6$	20249	18740	16792	15201	14040	13109	12051	11308	10574	9990	9444	8877
μ_{eff}[b]	3.65	3.73	3.88	4.00	4.12	4.23	4.28	4.35	4.39	4.45	4.53	4.57

Theoretical ($J = -35$ cm^{-1}, $g = 2.27$, $N\alpha = 450 \times 10^{-6}$)

T(K)	80	100	120	140	160	180	200	220	240	260	280	300
$\chi_M \times 10^6$	20375	17793	16285	14871	13697	12656	11770	10996	10315	9713	9176	8697

CuFe(aapen)Cl·H_2O

T(K)	81.1	95.7	115.6	135.4	155.2	175.1	195.1	215.2	235.6	256.0	275.6	295.4
$\chi_M \times 10^6$	55384	47029	39004	33252	29319	26058	23508	21452	19733	18231	17064	15918
μ_{eff}[a]	5.99	6.00	6.01	6.00	6.03	6.04	6.06	6.08	6.10	6.11	6.13	6.13

Ni_2(aapen)

T(K)	79.8	100.9	120.2	139.5	159.3	178.5	198.3	218.1	237.0	257.3	277.3	296.6
$\chi_M \times 10^6$	13027	10426	8606	7377	6534	5884	5296	4780	4430	4053	3801	3532
μ_{eff}[b]	2.88	2.90	2.88	2.87	2.89	2.90	2.90	2.89	2.90	2.89	2.90	2.89

NiCu(aapen)

T(K)	81.7	101.4	120.2	139.5	159.3	178.9	198.3	217.9	237.3	257.1	276.3	295.9
$\chi_M \times 10^6$	6144	4945	4338	3775	3449	3094	2916	2679	2560	2427	2264	2175
μ_{eff}[b]	2.00	2.00	2.04	2.05	2.10	2.10	2.15	2.16	2.20	2.23	2.24	2.27

NiCo(aapen)

T(K)	82.2	101.4	120.2	139.5	159.3	178.9	198.3	217.6	237.3	256.8	276.3	295.4
$\chi_M \times 10^6$	34993	27725	23251	19754	16847	14864	13434	12128	11071	10185	9414	8771
μ_{eff}[b]	4.80	4.74	4.73	4.69	4.63	4.61	4.61	4.59	4.58	4.57	4.56	4.55

NiFe(aapen)Cl

T(K)	81.7	98.3	118.4	138.3	158.2	178.2	198.0	217.9	237.6	257.3	277.1	296.4
$\chi_M \times 10^6$	51582	42551	35149	30316	26818	23965	21733	20079	18480	17244	16057	14991
μ_{eff}[b]	5.81	5.78	5.77	5.79	5.82	5.85	5.87	5.92	5.94	5.96	5.97	5.96

CuMn(aapen)(H_2O)$_2$

T(K)	83.4	105.0	126.9	147.4	168.5	189.3	210.7	232.8	253.4	274.3	295.4	
$\chi'_M \times 10^6$	15135	12158	10478	9374	8657	7991	7448	7081	6730	6398	6125	
μ_{eff}[b]	3.18	3.20	3.26	3.32	3.43	3.48	3.54	3.63	3.69	3.75	3.80	

NiMn(aapen)(H_2O)$_2$

T(K)	85.2	104.5	123.4	142.8	162.0	181.2	200.5	219.6	239.2	258.7	278.1	297.6
$\chi_M \times 10^6$	17895	15162	13329	11917	10816	9973	9203	8652	8249	7908	7479	7149
μ_{eff}[b]	3.49	3.56	3.63	3.69	3.74	3.80	3.84	3.90	3.97	4.04	4.09	4.12

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[a] Corrected for 8.5% paramagnetic impurity, whose susceptibility is estimated at 1450×10^{-6} c.g.s., e.m.u./mol at 300 °K.

[b] $\mu_{eff} = 2.828\,(\chi_M \cdot T)^{1/2}$.

The electronic spectrum of CuCo(aapen) shows the ligand field bands at 17500, 16300, 15600, 11900 and 8900 cm^{-1}. The band at 17500 cm^{-1} is attributable to the copper(II) in square planar geometry; the other bands may be due to the cobalt(II) ion. These data do not allow an unambiguous identification of the stereochemistry about the cobalt(II) ion.

The magnetic moment of CuCo(aapen) is 4.75 μ_B which seems common to a magnetically non-interacting Cu(II)–Co(II) system, taking into account the 1.63 μ_B of Cu(H_2aapen). The magnetic moment of a cobalt(II) ion in a tetrahedral symmetry is, generally, in the range 4.19–4.80 μ_B [21]. The magnetic moment of CuCo(aapen) depends on the temperature, indicating that a spin coupling between the two ions takes place. Assuming the Heisenberg model, the molar susceptibility for a copper(II) (s_1 = ½) + cobalt(II) (s_2 = 3/2) system is represented by the equation:

$$\chi_M = \frac{Ng^2\beta^2}{KT} \cdot \frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)} + N\alpha$$

where each symbol has the usual meaning. The magnetic susceptibility is in accordance with theoretical values when –J, g, Nα are 36 cm^{-1}, 2.27 and 450 × 10^{-6} esu/mol respectively. Similar values were found for a similar complex, CuCo(fsaen)·$3H_2O$ [8], in which an octahedral configuration was suggested.

The electronic spectrum of CuFe(aapen)Cl·H_2O shows only a broad band centered at 17,800 cm^{-1}, probably due to the overlapping of the charge transfer transition from ligand to Fe(III). The magnetic moment of the complex is 6.13 μ_B at 294.5 °K, very close to the magnetic moment of a high-spin Fe(III) ion under octahedral symmetry (5.9–6.2 μ_B) [21]. The magnetic moment slightly decreases with lowering temperature and follows the Curie–Weiss law with a small negative Weiss constant, indicating that only a very slight antiferromagnetic interaction is present between the Cu(II) and Fe(III) ions.

All the NiM′(aapen) (M′ = Ni, Cu, Co, Fe) complexes show a magnetic moment approximately constant in the temperature range examined, having μ_{eff} values corresponding to the mononuclear high-spin M′(H_2aapen)O_2O_2 complexes. These values may be explained on the assumption that the Ni(II) ion is square-planar coordinated and diamagnetic in all these complexes, consequently the entire paramagnetism arises from the second metal ion.

In reflectance spectra of the NiCo(aapen) and Ni_2(aapen) chelates the band around 17,000 cm^{-1} seems to correspond to the band for the mononuclear nickel(II) complex. Since square planar Ni(II) complexes have no absorption band at wavelengths than 600 nm, all the absorption bands in this region should be attributed to the second metal, Co(II) or Ni(II), in the O_2O_2 site. It is difficult to interprete these bands on the basis of a regular tetrahedral or planar coordination. We suggest for these ions, as for CuCo(aapen), a pseudotetrahedral geometry, which agrees well with their magnetic moments at room temperature (Table III).

The electronic spectrum of the NiFe(aapen)Cl complex does not provide dues for an understanding of the molecular structure; the d–d transitions for a s = 5/2 Fe(III) are very weak and the spectrum is dominated by a strong metal to ligand charge transfer band.

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