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SUPPORTING INFORMATION

Title: Tetranuclear Nickel Complexes Composed of Pairs of Dinuclear LNi_2 Fragments Linked by 4,4'-Bipyrazolyl, 1,4-Bis(4'-pyrazolyl)-benzene, and 4,4'-Bipyridazine: Synthesis, Structures, and Magnetic Properties
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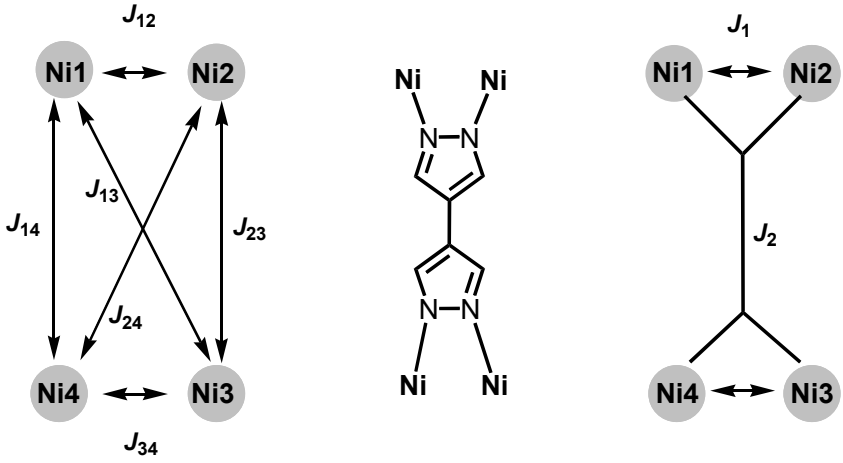
1) Derivation of the magnetic susceptibility expression for tetranuclear Ni complexes.
For a tetranuclear transition-metal complex, the spin Hamiltonian in zero field describing the isotropic interaction takes the form

$$H = -2J_{12}\hat{S}_1\hat{S}_2 - 2J_{13}\hat{S}_1\hat{S}_3 - 2J_{14}\hat{S}_1\hat{S}_4 - 2J_{23}\hat{S}_2\hat{S}_3 - 2J_{24}\hat{S}_2\hat{S}_4 - 2J_{34}\hat{S}_3\hat{S}_4 \qquad (1)$$

In the case of the compound described in this study eq. 2 can be rewritten as

$$H_{ex} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \qquad (2)$$

where J_1 (= J_{12} = J_{34}) relates to the interaction between the nickel(II) ions in the binuclear subunit and J_2 (=J_{14} = J_{23} = J_{24} = J_{34}) indicates the spin exchange integral involving the metal ions bridged by the bipyrazolate group.



The complete matrix of H can be calculated by writing out the coupled states and determining the matrix elements by elementary operations with angular momenta operators (see E. Sinn, *Coord. Chem. Rev.*, **1970**, *5*, 313–347 and P. W. Atkins, *Molecular Quantum Mechanics*, 2nd ed., Oxford University Press, Oxford, **1983**).

If additional terms due to the Zeeman splitting and single-ion zero-field splitting are considered, the Hamitonian takes the form

$$H = H_{ex} + \sum_i [D_i(\hat{S}_{iz}^2 - \tfrac{1}{3}S_i(S_i+1)) + g_i\mu_B B_\tau \hat{S}_{i\tau}] \ (\tau = x, y, z) \qquad (3)$$

The resulting Hamiltonian matrix is diagonalized numerically for given values of J_1, J_2, g and D. The slope of E versus B is calculated at the desired field; this slope is the magnetic moment for the ith energy level. The molar paramagnetic susceptibility, χ, of the system is then calculated as a function of temperature using equation 4,

$$\chi = \chi_{tetra}(1-\rho) + 4\chi_{mono}\rho \qquad (4)$$

where χ_{tetra} and χ_{mono} refer to the molar susceptibilities of the tetranuclear complex and a fraction ρ of a mononuclear nickel(II) impurity:

$$\chi_{tetra} = \frac{N}{B_0} \frac{\sum_i (-\partial E_i / \partial B) \exp(-E_i / kT)}{\sum_i \exp(-E_i / kT)}$$

$$\chi_{mono} = \frac{Ng^2 \mu_B^2}{3kT} \left(\frac{2}{2} \left(\frac{2}{2} + 1 \right) \right)$$

A least squares program (routines were taken from W. H. Press, W. T. Vetterling, S. A. Teukolsky, B. P. Flannery, *NUMERICAL RECIPES IN C: The Art of Scientific Computing*, Cambridge University Press, Cambridge, **1992**) then compares calculated and observed susceptibility curves and changes the parameters to get the best fit.

a) The experimental and calculated data for complex **9**$[BPh_4]_2$ are as follows:

T	μ_{eff}/μ_B	μ_{calc}/μ_B
295.0333	6.7500	6.7850
289.5795	6.7761	6.7890
284.6604	6.7816	6.7929
279.5742	6.7861	6.7970
274.5798	6.7903	6.8013
269.5553	6.7949	6.8059
264.5589	6.8016	6.8106
259.5562	6.8081	6.8157
254.5584	6.8127	6.8209
249.5691	6.8188	6.8264
244.5719	6.8249	6.8322
239.5722	6.8302	6.8383
234.5833	6.8369	6.8447
229.5745	6.8433	6.8515
224.5913	6.8522	6.8585

219.5906	6.8600	6.8659
214.5893	6.8686	6.8737
209.5934	6.8773	6.8819
204.6108	6.8865	6.8905
199.6232	6.8955	6.8995
194.6133	6.9062	6.9090
189.6281	6.9151	6.9190
184.6430	6.9272	6.9294
179.6564	6.9387	6.9404
174.6747	6.9489	6.9520
169.6840	6.9596	6.9641
164.7056	6.9739	6.9769
159.7217	6.9883	6.9903
154.7504	7.0012	7.0044
149.7542	7.0173	7.0193
144.7907	7.0339	7.0349
139.8006	7.0507	7.0514
134.8286	7.0677	7.0687
129.8514	7.0868	7.0869
124.8678	7.1037	7.1060
119.8846	7.1234	7.1261
114.9178	7.1454	7.1472
109.9284	7.1680	7.1694
104.9407	7.1928	7.1927
100.0239	7.1817	7.2167
94.9779	7.2229	7.2424
89.9839	7.2512	7.2689
84.9960	7.2815	7.2964
80.0032	7.3125	7.3248
75.0126	7.3420	7.3539
70.0295	7.3728	7.3834
65.0389	7.3953	7.4132
60.0621	7.4304	7.4427

55.0467	7.4549	7.4716
50.0532	7.4910	7.4987
48.0150	7.5016	7.5091
46.0390	7.5128	7.5188
44.0287	7.5240	7.5281
42.0224	7.5347	7.5367
40.0128	7.5448	7.5447
38.0048	7.5540	7.5520
36.0039	7.5629	7.5583
33.9981	7.5702	7.5638
31.9973	7.5769	7.5684
29.9956	7.5823	7.5719
27.9950	7.5864	7.5744
25.9941	7.5873	7.5757
23.9921	7.5871	7.5760
21.9989	7.5875	7.5752
20.0001	7.5830	7.5732
19.0009	7.5806	7.5718
18.0006	7.5778	7.5700
17.0001	7.5745	7.5678
16.0020	7.5705	7.5653
15.0005	7.5654	7.5622
13.9995	7.5584	7.5586
12.9984	7.5473	7.5542
11.9953	7.5329	7.5488
10.9844	7.5365	7.5422
9.9993	7.5302	7.5339
9.0006	7.5152	7.5231
8.0010	7.4981	7.5087
7.0033	7.4729	7.4887
6.0116	7.4397	7.4601
4.9991	7.3814	7.4155
3.9921	7.3194	7.3430

2.9990	7.2125	7.2152
1.9976	6.9726	6.9444

The parameters resulting from the best least-squares fit to the data are $J_1 = 23.97$ cm^{-1}, $J_2 = -0.0011$ cm^{-1}, $g = 2.19$, $D = 4.77$ cm^{-1} and $\rho = 0.02$ %.

2) Derivation of the magnetic susceptibility expression for 9[BPh$_4$]$_2$ (dinuclear model).

The derivation of the magnetic suceptibility expression including single-ion zero-field splitting effects for a dinuclear nickel(II) complex under the spin Hamiltonian in eq. 5 is summarized below.

$$H = -2JS_1S_2 + \sum_{i=1}^{2}(D_i(\widehat{S}_{zi}^2 - 1/3(S_i(S_i+1)) + g_i\mu_B S_{i\tau}B_\tau)) \quad (\tau = x, y, z) \qquad (5)$$

The complete matrix of H can be calculated by writing out the coupled states and determining the matrix elements by elementary operations with angular momenta operators (see P. W. Atkins, *Molecular Quantum Mechanics*, 2nd ed., Oxford University Press, Oxford, **1983**). Diagonalization of the Hamiltonian matrix gives the energies of each of the 9 eigenfunctions for given values of J, D, B and g. The molar paramagnetic susceptibility, χ, was calculated with equation 6,

$$\chi = 2[\chi_{\mathrm{dim}}(1-\rho) + 2\chi_{mono}\rho] \qquad (6)$$

where

$$\chi_{\mathrm{dim}} = \frac{N}{B_0}\frac{\sum_i(-\partial E_i/\partial B)\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

and

$$\chi_{mono} = \frac{Ng^2\mu_B^2}{3kT}\left(\frac{2}{2}\left(\frac{2}{2}+1\right)\right)$$

by assuming a molar fraction ρ of an uncoupled paramagnetic impurity (a mononuclear Ni^{II} complex). A least squares program then compares calculated and observed susceptibility curves and changes the parameters to get the best fit.

a) The experimental and calculated data for complex **9**[BPh$_4$]$_2$ are as follows:

T	μ_{eff}/μ_B	μ_{calc}/μ_B
295.0333	6.7500	6.7595
289.5795	6.7761	6.7644
284.6604	6.7816	6.7690
279.5742	6.7861	6.7740
274.5798	6.7903	6.7791
269.5553	6.7949	6.7844
264.5589	6.8016	6.7900
259.5562	6.8081	6.7958
254.5584	6.8127	6.8018
249.5691	6.8188	6.8081
244.5719	6.8249	6.8146
239.5722	6.8302	6.8215
234.5833	6.8369	6.8286
229.5745	6.8433	6.8361
224.5913	6.8522	6.8439
219.5906	6.8600	6.8521
214.5893	6.8686	6.8606
209.5934	6.8773	6.8695
204.6108	6.8865	6.8788
199.6232	6.8955	6.8885
194.6133	6.9062	6.8988
189.6281	6.9151	6.9094
184.6430	6.9272	6.9206
179.6564	6.9387	6.9322
174.6747	6.9489	6.9444
169.6840	6.9596	6.9573
164.7056	6.9739	6.9707
159.7217	6.9883	6.9847
154.7504	7.0012	6.9994
149.7542	7.0173	7.0150
144.7907	7.0339	7.0311
139.8006	7.0507	7.0482

134.8286	7.0677	7.0660
129.8514	7.0868	7.0847
124.8678	7.1037	7.1043
119.8846	7.1234	7.1249
114.9178	7.1454	7.1464
109.9284	7.1680	7.1691
104.9407	7.1928	7.1927
100.0239	7.1817	7.2170
94.9779	7.2229	7.2431
89.9839	7.2512	7.2698
84.9960	7.2815	7.2975
80.0032	7.3125	7.3260
75.0126	7.3420	7.3552
70.0295	7.3728	7.3848
65.0389	7.3953	7.4146
60.0621	7.4304	7.4440
55.0467	7.4549	7.4727
50.0532	7.4910	7.4996
48.0150	7.5016	7.5099
46.0390	7.5128	7.5195
44.0287	7.5240	7.5287
42.0224	7.5347	7.5372
40.0128	7.5448	7.5451
38.0048	7.5540	7.5522
36.0039	7.5629	7.5585
33.9981	7.5702	7.5639
31.9973	7.5769	7.5683
29.9956	7.5823	7.5718
27.9950	7.5864	7.5742
25.9941	7.5873	7.5756
23.9921	7.5871	7.5758
21.9989	7.5875	7.5750
20.0001	7.5830	7.5731

19.0009	7.5806	7.5716
18.0006	7.5778	7.5699
17.0001	7.5745	7.5678
16.0020	7.5705	7.5652
15.0005	7.5654	7.5622
13.9995	7.5584	7.5586
12.9984	7.5473	7.5543
11.9953	7.5329	7.5490
10.9844	7.5365	7.5424
9.9993	7.5302	7.5342
9.0006	7.5152	7.5234
8.0010	7.4981	7.5090
7.0033	7.4729	7.4890
6.0116	7.4397	7.4603
4.9991	7.3814	7.4157
3.9921	7.3194	7.3430
2.9990	7.2125	7.2149
1.9976	6.9726	6.9428

The parameters resulting from least-squares for the data are $J = 24.14$ cm^{-1}, $g = 2.19$, $D = 4.85$ cm^{-1}, and $\rho = 0.02$ %.