

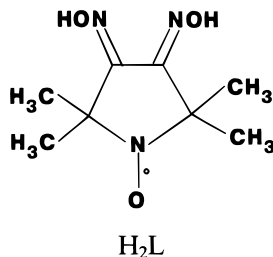
## Nonclassical Packing of Metal Dioximates. Superexchange through a Diamagnetic Metal Cation

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Received December 4, 1997

It is well-known that Ni(II) and Pd(II) dioximates show stacking effects in the solid state.<sup>1</sup> This prompted us to attempt to synthesize a spin-labeled stacking polymer from Ni(II) and Pd(II) complexes with a stable nitroxide 2,2,5,5-tetramethyl-1-oxylpyrrolidine-3,4-dione dioxime (H<sub>2</sub>L) and investigate its



magnetic properties. The spin-labeled dioxime molecule H<sub>2</sub>L seemed to be very suitable for solving this problem, because it consists of only the necessary fragments—a sterically hindered nitroxyl group and a vicinal dioxime group. The cyclic structure of the H<sub>2</sub>L molecule and the methyl substituents in the  $\alpha$ -positions relative to the carbon atoms of the oxime groups do not hinder stacking, which is possible in solid Ni(II) and Pd(II) complexes formed from ordinary diamagnetic cyclic dioximes and dioximes with branched substituents.<sup>2–7</sup> Moreover, earlier it was found that M(HL)<sub>2</sub> molecules, where M is Ni(II) or Pd(II), are square planar in solution and thus favor formation of stacked structures. In M(HL)<sub>2</sub> solutions, exchange interactions were studied by investigating extraction of metal ion solutions with spin-labeled dioximes by ESR.<sup>8,9</sup> Solid M(HL)<sub>2</sub> complexes were not isolated and investigated.

We succeeded in isolating M(HL)<sub>2</sub> as individual solids, including single crystals suitable for an X-ray diffraction analysis. Ni(HL)<sub>2</sub> was synthesized by the reaction of Ni(CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> and H<sub>2</sub>L in methanol in the presence of an Et<sub>3</sub>N excess. Pd(HL)<sub>2</sub> was obtained by the reaction of a methanol solution of H<sub>2</sub>L with an aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> in the presence of an

Et<sub>3</sub>N excess with subsequent extraction of the product with CHCl<sub>3</sub>.<sup>10</sup> Under the conditions of the synthesis, M(HL)<sub>2</sub> complexes are isolated as analytically pure finely dispersed powders. Like bischelates with ordinary diamagnetic dioximes, M(HL)<sub>2</sub> is insoluble in water and alcohols. CHCl<sub>3</sub> is the best solvent for these compounds, although their solubility in it is very limited (at 295 K the maximal concentrations are  $1.09 \times 10^{-3}$  and  $1.49 \times 10^{-2}$  M for Ni(HL)<sub>2</sub> and Pd(HL)<sub>2</sub>, respectively).

Our investigation of Ni(HL)<sub>2</sub> and Pd(HL)<sub>2</sub> single crystals unexpectedly revealed a layered polymeric structure of the solids.<sup>11</sup> Figure 1 shows the structure of the Ni(HL)<sub>2</sub> molecule, and Figure 2 presents the structure of a polymeric layer. The centrosymmetric square planar environment of the metal consists of the nitrogen atoms of the oxime groups. The metallocycles as well as the imidazoline heterocycles are virtually planar (the rms deviations of atoms are no more than 0.03 Å). The ML<sub>2</sub> molecules have intramolecular hydrogen bonds O–H...O, which are typical in dioximates. The square planar environment of the metal is completed to distorted octahedral by the O atoms of the N–O groups of neighboring molecules (Figure 2). This leads to formation of a parquet-like layered polymer structure of the solid. The layers lie parallel to the (100) plane. The angles between the planes of the coordination squares and the additional M–O bonds are 155.6 and 159.4° for NiL<sub>2</sub> and PdL<sub>2</sub>, respectively. We failed to find any references to Ni(II) and Pd(II) dioximates possessing a layered polymer structure.<sup>12</sup> We believe that M(HL)<sub>2</sub> are the first examples of layered polymer Ni(II) and Pd(II) dioximates with a parquet packing of molecules in the solid state.

The layered polymer structure of M(HL)<sub>2</sub> is responsible for the formation of exchange clusters  $>N\cdots O\cdots M\cdots O\cdots N<$ , where

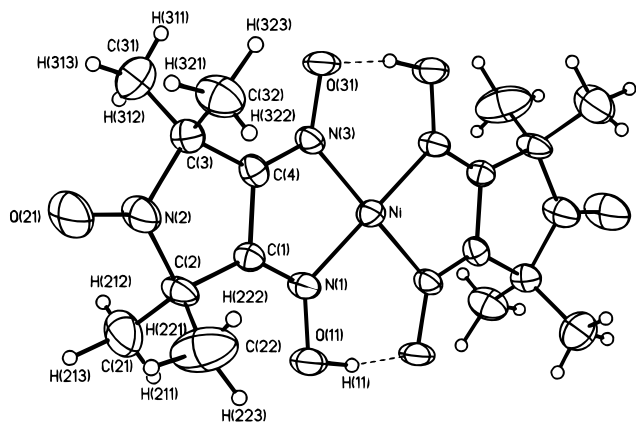
(10) Satisfactory analyses were obtained. Synthetic procedures and analytical data for the complexes are deposited as Supporting Information.

(11) X-ray data for NiL<sub>2</sub> (C<sub>16</sub>H<sub>26</sub>N<sub>6</sub>NiO<sub>6</sub>): yellow plate, fw 457.14, monoclinic, P2<sub>1</sub>/c (No. 19) at 293 K;  $a = 8.067(1)$  Å,  $b = 11.312(1)$  Å,  $c = 11.863(1)$  Å,  $\beta = 108.92(1)^\circ$ ,  $V = 1024.0(2)(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $d(\text{calc}) = 1.483$  g/cm<sup>3</sup>. Data were collected on a Siemens P3 automatic diffractometer with the  $\theta/2\theta$  scan technique in the range  $2.56 \leq \theta \leq 25.05^\circ$  (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.993$  mm<sup>-1</sup>;  $0 < h < 9$ ,  $0 < k < 13$ ,  $-14 < l < 13$ ). A total of 1952 reflections gave 1818 unique ones with  $R_{\text{int}} = 0.0483$ , which were used in the refinement. Final  $R$  indices:  $R_1 = 0.0757$ ,  $wR_2 = 0.0666$  for 1818  $I_{hkl} > 2\sigma_I$  and  $R_1 = 0.1797$ ,  $wR_2 = 0.0827$  for all data, GOF = 1.125, extinction coefficient = 0.0007(11). X-ray data for PdL<sub>2</sub> (C<sub>16</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub>Pd): orange plate, fw 504.83, monoclinic, P2<sub>1</sub>/c (No. 19) at 293 K;  $a = 8.079(2)$  Å,  $b = 11.329(2)$  Å,  $c = 12.078(2)$  Å,  $\beta = 109.91(2)^\circ$ ,  $V = 1039.6(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $d(\text{calc}) = 1.613$  g/cm<sup>3</sup>. Data were collected on a Siemens P3 automatic diffractometer with the  $\theta/2\theta$  scan technique in the range  $3.22 \leq \theta \leq 27.05^\circ$  (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.938$  mm<sup>-1</sup>;  $0 < h < 9$ ,  $0 < k < 14$ ,  $-15 < l < 14$ ). A total of 2173 reflections gave 2014 unique ones with  $R_{\text{int}} = 0.0244$ , which were used in the refinement. Final  $R$  indices:  $R_1 = 0.0326$ ,  $wR_2 = 0.0696$  for 2014  $I_{hkl} > 2\sigma_I$  and  $R_1 = 0.0531$ ,  $wR_2 = 0.0802$  for all data, GOF = 1.098, extinction coefficient = 0.0020(6). Both structures were solved by direct methods using SHELXS-86 and refined anisotropically for all non-hydrogen atoms. H atoms were located on a difference  $F$  map and included in the refinement in an isotropic approach. The refinement was performed on  $F^2$  by the full-matrix least-squares method (SHELXL-97).

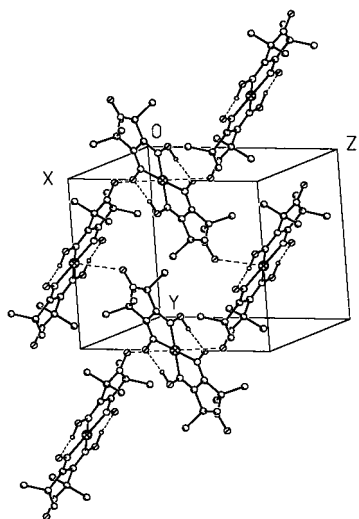
(12) Cambridge Crystallographic Database System, Database Version 5.14; October 1997 release.

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- (1) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.
- (2) Leichert, I.; Weiss, J. *Acta Crystallogr.* **1975**, *31*, 2877.
- (3) Brown, L. D.; Kalina, D. W.; McClure, M. S.; Schulz, S.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2937.
- (4) Bowers, R. H.; Banks, C. V.; Jacobson, R. A. *Acta Crystallogr., Sect. B* **1972**, *28*, 2318.
- (5) Cowie, M.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2921.
- (6) Nuvan, L. A.; Brianso, J. L.; Solans, X.; Font-Altaba, M.; De Matheus, M. *Acta Crystallogr., Sect. C* **1983**, *39*, 211.
- (7) Hussain, M. S. *Acta Crystallogr., Sect. A* **1984**, *40*, C290.
- (8) Evstiferov, M. V.; Vanifatova, N. G.; Kokorin, A. I.; Petrukhin, O. M.; Voldarskii, L. B.; Zolotov, Yu. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 2489.
- (9) Evstiferov, M. V.; Vanifatova, N. G.; Petrukhin, O. M.; Kokorin, A. I.; Voldarskii, L. B.; Zolotov, Yu. A. *International Solvent Extraction Conference. Moscow, July 18–24, 1988. Conference Papers*; Nauka, Moscow, 1988; Vol. 1, p 95.

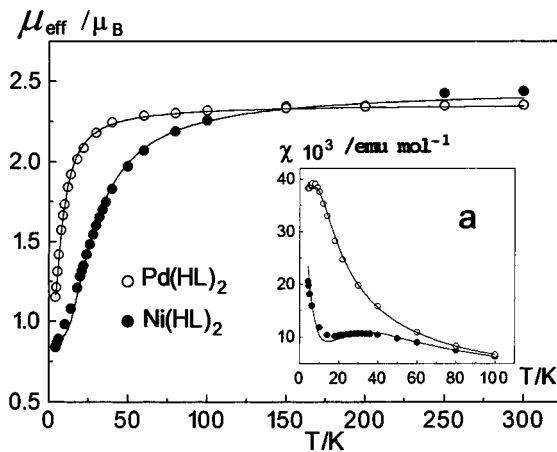


**Figure 1.** Atomic numbering scheme in the  $\text{NiL}_2$  molecule. Thermal ellipsoids are drawn at 50% probability. Selected distances ( $\text{\AA}$ ) and angle (deg): Ni–N(1) 1.876(4), Ni–N(3) 1.886(4), N(3)–C(4) 1.283(5), N(3)–O(31) 1.340(4), C(4)–C(1) 1.464(6), C(4)–C(3) 1.510(7), C(3)–N(2) 1.499(6), C(3)–C(31) 1.505(8), C(3)–C(32) 1.518(8), N(2)–O(21) 1.266(5), N(2)–C(2) 1.485(7), C(2)–C(1) 1.482(7), C(2)–C(22) 1.515(10), C(2)–C(21) 1.516(9), C(1)–N(1) 1.292(5), N(1)–O(11) 1.340(5), O(11)–H(11) 1.01(7); N(1)–Ni–N(3) 84.6(2). The structure of the  $\text{PdL}_2$  molecule and atomic numbering scheme are the same. Selected distances ( $\text{\AA}$ ) and angle (deg) for  $\text{PdL}_2$ : Pd–N(1) 1.982(3), Pd–N(3) 1.990(3), N(1)–C(1) 1.292(5), N(1)–O(11) 1.342(4), C(1)–C(4) 1.454(5), C(1)–C(2) 1.497(5), C(2)–N(2) 1.492(5), C(2)–C(21) 1.513(7), C(2)–C(22) 1.530(7), N(2)–O(21) 1.266(4), N(2)–C(3) 1.507(5), C(3)–C(4) 1.504(5), C(3)–C(31) 1.528(6), C(3)–C(32) 1.520(6), C(4)–N(3) 1.294(5), N(3)–O(31) 1.333(4), O(11)–H(11) 0.99(9); N(1)–Pd–N(3) 81.9(1).



**Figure 2.** Packing of  $\text{ML}_2$  molecules in the unit cell. Intramolecular H-bond distances O(11)–H(11)···O(31') (O–H, H···O, O···O,  $\angle\text{OHO}$ : 1.01(7)  $\text{\AA}$ , 1.49(7)  $\text{\AA}$ , 2.483(5)  $\text{\AA}$ , 168(6) $^\circ$  for  $\text{NiL}_2$ ; 0.99(9)  $\text{\AA}$ , 1.74(10)  $\text{\AA}$ , 2.683(4)  $\text{\AA}$ , 159(9) $^\circ$  for  $\text{PdL}_2$ ) and intermolecular contacts  $\text{M}\cdots\text{O}\cdots(\text{Ni}\cdots\text{O}(21'))$  2.953(4)  $\text{\AA}$ ,  $\text{Pd}\cdots\text{O}(21')$  3.226(4)  $\text{\AA}$ ) are given by broken lines.

M is the diamagnetic metal ion. The  $\text{M}\cdots\text{O}\cdots$  distances (2.953  $\text{\AA}$  for  $\text{Ni}(\text{HL})_2$  and 3.226  $\text{\AA}$  for  $\text{Pd}(\text{HL})_2$ ) are long enough for the energies of  $\text{M}\cdots\text{O}\cdots$  interactions to be considered comparable to the energies of normal chemical bonds. At the same time, these distances are short enough for effective interactions between the magnetic orbitals of the nitroxyl groups of different molecules via the intermediate metal ion separating the  $>\text{N}\cdots\text{O}$  groups. The experimental temperature dependences of magnetic susceptibility of  $\text{M}(\text{HL})_2$  (Figure 3) are very well fitted by the Bleaney–Bowers model for isolated two-center exchange clusters with spin  $1/2$ .<sup>13</sup> It was determined that the intermolecular exchange in solid Ni-



**Figure 3.** Plots of magnetic moments and magnetic susceptibilities (insert a) vs temperature for  $\text{M}(\text{HL})_2$ . The solid lines represent the calculated values with the best fit parameters.

$(\text{HL})_2$  is much more significant than that in solid  $\text{Pd}(\text{HL})_2$ :  $J = -22.3 \text{ cm}^{-1}$  (in an  $\hat{H} = -2J\hat{S}_1\hat{S}_2$  Hamiltonian) for  $\text{Ni}(\text{HL})_2$  and  $-6.5 \text{ cm}^{-1}$  for  $\text{Pd}(\text{HL})_2$ . The  $>\text{N}\cdots\text{O}\cdots\text{M}\cdots\text{O}\cdots\text{N}<$  fragments (Figure 2) form exchange clusters in  $\text{M}(\text{HL})_2$  solids.<sup>14</sup> Lengthening of  $\text{M}\cdots\text{O}\cdots$  distances in  $\text{Pd}(\text{HL})_2$  as compared to those in  $\text{Ni}(\text{HL})_2$  (3.226 and 2.953  $\text{\AA}$ , respectively) decreases the exchange interaction energies ( $-6.5$  and  $-22.3 \text{ cm}^{-1}$ , respectively). The structures of  $\text{Ni}(\text{HL})_2$  and  $\text{Pd}(\text{HL})_2$  clearly demonstrate the efficiency of spin interactions through the bridging diamagnetic metal ion. In the absence of a diamagnetic metal ion, the exchange interactions between the unpaired electrons of  $\text{N}\cdots\text{O}$  groups separated by 6  $\text{\AA}$  are not more than  $1 \text{ cm}^{-1}$ .<sup>15,16</sup> In fact, superexchange in the  $>\text{N}\cdots\text{O}\cdots\text{O}\cdots\text{N}<$  fragments of solid  $\text{M}(\text{HL})_2$  gives an antisymmetrical picture of classical superexchange in  $\text{M}\cdots\text{X}\cdots\text{M}$  fragments, where unpaired electrons of two paramagnetic metal ions (M) interact through the diamagnetic ligand (X).<sup>17</sup>

Thus studies of the magnetic properties of solid  $\text{Ni}(\text{HL})_2$  and  $\text{Pd}(\text{HL})_2$  established a rather high efficiency of the bridging diamagnetic metal ion in “conducting” exchange interactions. It is reasonable to take into account this circumstance together with the known data for molecular dinuclear clusters where a substantial interaction between two nitroxides is propagated through two diamagnetic metal ions<sup>18–20</sup> in the design of molecular ferromagnets.

**Acknowledgment.** The authors express their gratitude to INTAS (Grant 94-3508), RFBR (Grants 96-03-32229 and 96-07-89187), and the Ministry of Science and Technologies of Russia for financial support.

**Supporting Information Available:** Text giving the synthetic procedures for  $\text{Ni}(\text{HL})_2$  and  $\text{Pd}(\text{HL})_2$  (1 page). X-ray crystallographic files, in CIF format are available on the Internet only. Ordering and access information is given on any current masthead page.

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- (14) It was established that in solution the magnetic properties of the  $\text{Ni}(\text{HL})_2$  and  $\text{Pd}(\text{HL})_2$  biradicals are very similar and in the bischelat molecules the intramolecular exchange energies are fairly low and equal to 26.5 and 36.8 G, respectively (for details, see refs 8, 9).
- (15) Caneschi, A.; Gatteschi, D.; Rey, P. *Prog. Inorg. Chem.* **1991**, *39*, 331.
- (16) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
- (17) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.
- (18) Dong, T.-Y.; Hendrickson, D. N.; Felthouse, T. R.; Shieh, H.-S. *J. Am. Chem. Soc.* **1984**, *106*, 5373.
- (19) Felthouse, T. R.; Dong, T.-Y.; Hendrickson, D. N.; Shieh, H.-S.; Thompson, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 8201.
- (20) Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1989**, *111*, 3230.

(13) Bleaney, B.; Bowers, K. D. *Proc. R. Soc.* **1952**, *A214*, 451.