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Metal–Metal Interactions

Structural, Magnetic, and Theoretical Characterization of a Heterometallic Polypyridylamide Complex**

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One-dimensional complexes with metal-containing backbones have been attractive to physicists and chemists for several decades,[1] and their interest has been further increased in the last ten years by potential applications in nanoelectronics.[2] Apart from the family of platinum and iridium blues, most chains of metal atoms were constrained to be aligned by means of purposely designed ligands.[3,4] The polypyridylamido ligands have produced to date the widest variety of metal chains with controlled lengths, as far as the nature and the number of metal atoms are concerned.[3] Strings with three to nine metal atoms were obtained with Cr and Ni. Chains containing three or five metal atoms, characterized for Co, Cu, Ru, and Rh, have unprecedented structural versatility and magnetic behavior that is hard to predict.[3] Even though heterometallic chain complexes are not uncommon[5] and often exhibit similarity to platinum blues[6] or involve weak noncovalent interactions between heavy atoms,[7] all linear complexes with polypyridylamido or closely related ligands characterized to date incorporate a single type of metal atoms. We report here the synthesis, X-ray structure, and magnetic properties of $[Co_2PdCl_2(dpa)_4]$ (**1**; dpa = bis(2-pyridyl)amide), the first trinuclear complex of dpa with a heteronuclear backbone. The magnetic behavior of **1** was investigated and found to be consistent with a complex interaction involving zero-field splitting superimposed on strong exchange coupling between two high-spin Co^{II} ions separated by a diamagnetic Pd center. The ground-state electronic structure of **1** was interpreted by means of DFT calculations.

Complex **1** was synthesized by a variant of the protocol currently used to obtain trinuclear dipyridylamide complexes.[8] Single-crystal X-ray analysis of $\mathbf{1}\cdot(C_2H_5)_2O$ resulted in the structure displayed in Figure 1. The heterometallic chain is helically wrapped by four *syn–syn*-type ligands, and the complex exhibits approximate D_4 symmetry. The average Co–N (2.16 Å) and Co–Cl (2.34 Å) distances are quite similar to those observed at room temperature for the isolated, high-spin Co^{II} ion in the unsymmetrical form of $[Co_3Cl_2(dpa)_4]$.[9] The average Pd–N (2.01 Å) is much shorter than the average Co–N distance and suggests that the Pd atom is essentially low-spin ($S = 0$) in square-planar coordination. The relatively short Pd–Co distance (2.52 Å) is consistent with a weak metal–metal interaction, as confirmed by DFT calculations.

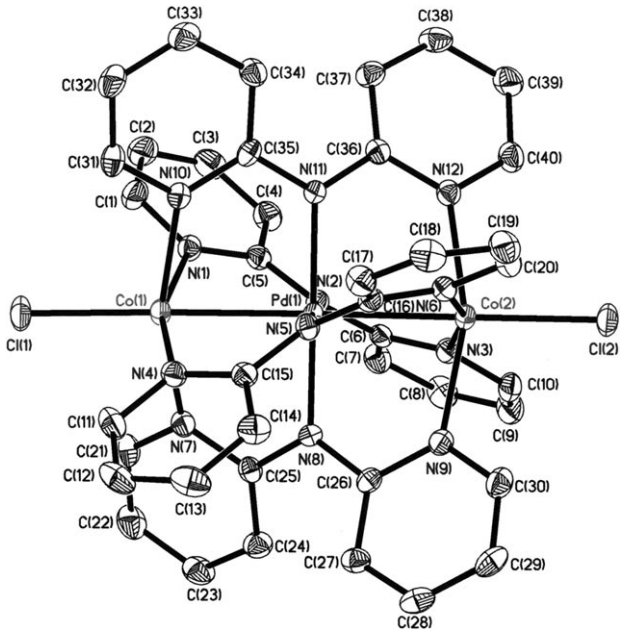

Figure 1. ORTEP view of the molecular structure of **1** (50% probability). Selected interatomic distances (averaged): Co–Pd 2.52, Co–Cl 2.34, Co–N 2.16, Pd–N 2.01 Å.

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The temperature-dependent magnetic susceptibility of **1** was investigated (Figure 2). With decreasing temperature, the $\chi_M T$ value decreases rapidly in an unusual linear fashion. This behavior can be ascribed to an antiferromagnetic interaction

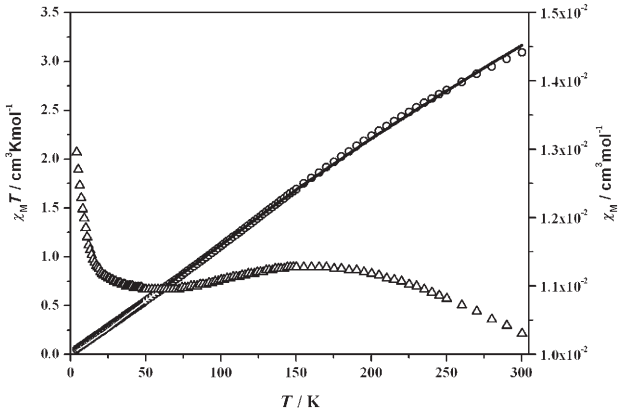

Figure 2. Temperature dependence of $\chi_M T$ (○) and χ_M (△) of **1**. The black line shows the best fit of $\chi_M T$ (see text). The χ_M data below 25 K are probably affected by a paramagnetic impurity.

modified by the contribution of anisotropic exchange. The $\chi_M T$ value at 300 K ($3.09\ cm^3 K mol^{-1}$) is smaller than expected for two isolated $S = 3/2$ spins ($3.75\ cm^3 K mol^{-1}$), and this can be interpreted as resulting from significant antiferromagnetic coupling. A satisfactory fit (Figure 2) was obtained with a model including the isotropic Heisenberg Hamiltonian plus an axial zero-field splitting operator [Eq. (1)].[10]

$$\hat{H} = -2J\,\hat{S}_1\,\hat{S}_2 + D\left[\hat{S}_z^2 - {}^1/_3 S(S+1)\right] \qquad (1)$$

The best-fit parameters are $g = 2.20$, $2J = -92.47\ cm^{-1}$, $|D| = 50.95\ cm^{-1}$, $\chi_{TIP} = 0.01\ cm^3 mol^{-1}$, and $R^2 = 0.99$. The temperature-independent paramagnetism (TIP) was included in this fitting procesure to describe the coupling between ground and ecited states. The value obtained for $|D|$ is similar to those derived for various five- or six-coordinate high-spin mono- and dicobalt(II) complexes.[10] The data measured for χ_M below 25 K varied significantly with the sample and gave rise to a sharp increase in χ_M that should be assigned to the presence of a paramagnetic impurity in variable amounts.

The DFT/B3LYP calculations were carried out on **1** with the Gaussian 03 software package.[11] Previous calculations on the symmetric (*s*) form of $[Co_3Cl_2(dpa)_4]$ and other $[M_3Cl_2(dpa)_4]$ complexes[12] have clarified the shape and the sequence of the metal orbitals in these complexes under the assumption of D_4 symmetry (Figure 3).

In the molecular ground state, the occupancies of the highest MOs depend on the competition between the scheme of a metal chain exhibiting a strong, delocalized interaction, and that of an assembly of weakly interacting metal atoms. Various electronic configurations referring to both models were computed for **1**, and their geometries optimized. For

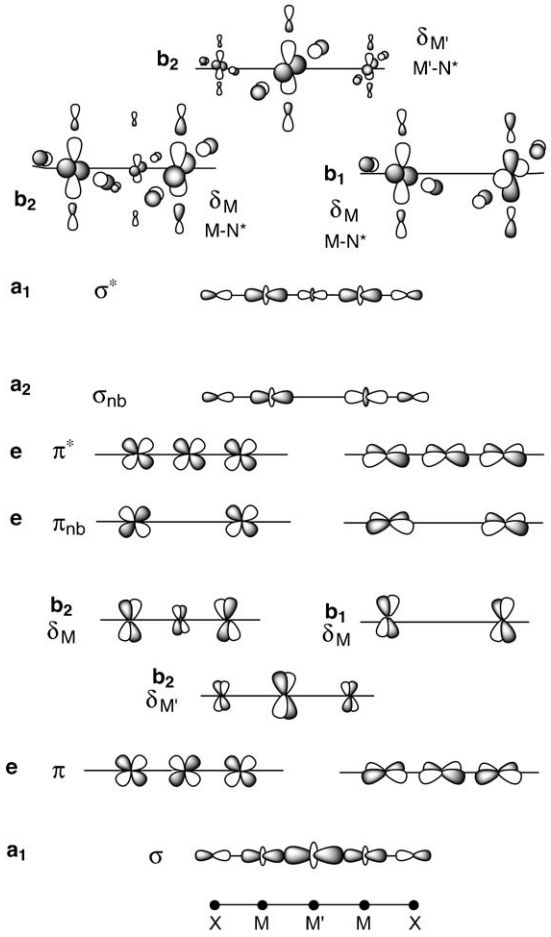

Figure 3. Sequence of metal orbitals in the closed-shell electronic configurations of *s*-$[Co_3Cl_2(dpa)_4]$ and $[Co_2PdCl_2(dpa)_4]$ (D_4 symmetry).

each configuration, Figure 4 displays the distribution of the metal electrons among the 15 metal valence orbitals, together with the relative energy of each configuration. The main geometrical parameters associated with each configuration are given in the Supporting Information.

In agreement with the latter model, the magnetic behavior observed for **1** suggests that the ground state results from antiferromagnetic coupling between two high-spin ($S = 3/2$) Co^{II} ions, separated by a magnetically inactive Pd^{II} center. The resulting molecular state of maximal spin is therefore a septet ($^7A_2$) with six unpaired electrons largely localized on the terminal metal atoms. This state was indeed found to be lowest in energy in symmetry-adapted calculations, that is, without considering any magnetic coupling between unpaired electrons (Figure 4). The geometry optimized for the $^7A_2$ state agrees well with the observed structure. For the two other electronic states displayed in Figure 4, the optimal distances are strongly at variance with experiment (Supporting Information).

As long as the electronic ground state of the magnetic centers is nondegenerate, coupling between spins S_1 and S_2 of two transition metals is appropriately modeled by means of the isotropic Heisenberg Hamiltonian $\hat{H} = -2J_{12}\hat{S}_1 \cdot \hat{S}_2$. The case of high-spin Co^{II} ($^4T_{1g}$ state) is more complicated,

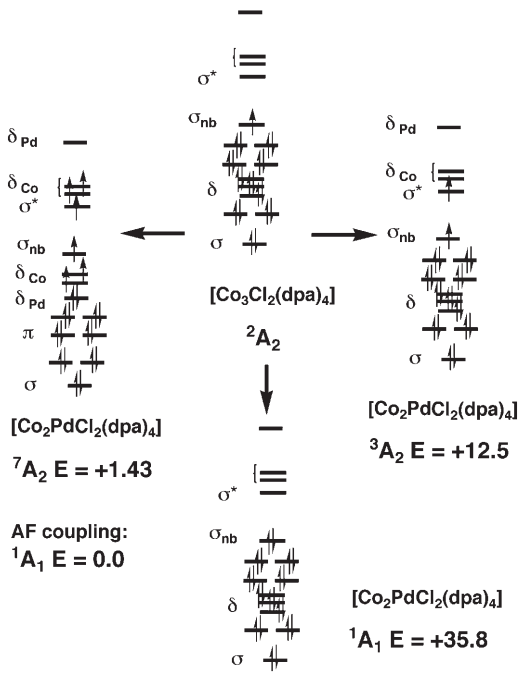

Figure 4. Lowest electronic configuration for *s*-$[Co_3Cl_2(dpa)_4]$ and three competing electronic configurations for **1**. Relative energies [kcal mol^{-1}] are given with respect to the broken-symmetry state resulting from antiferromagnetic (AF) coupling of six unpaired electrons.

however, due to the combination of orbital and spin degeneracies. A convenient treatment requires the introduction of spin–orbit coupling terms in the expression of the Hamiltonian, which then becomes symmetry-dependent.[10,13] Most recent treatments of magnetic susceptibility rely on the assumption that the isotropic exchange coupling is small compared to the energy gap between the lowest energy levels generated from the $^4T_{1g}$ atomic ground state by spin–orbit coupling.[14–16] To our knowledge, all dinuclear Co^{II} complexes with atomic spins 3/2 investigated to date satisfy the latter condition, with $-2J$ values of less than 20 cm^{-1}.[13,14,16]

The development of a complete theoretical analysis of the magnetism in **1** is far beyond the scope of this communication. However, within the framework of the present DFT/B3LYP calculations, we can provide a rough estimate of the exchange coupling parameter, assumed to be isotropic. The method used for this calculation is the broken-symmetry (BS) approach of Noodleman et al.,[17] based on the classical Heisenberg Hamiltonian. This method does not account for the orbitally dependent corrections to the exchange interactions.[14]

The unpaired electrons localized on the Co atoms in the $^7A_2$ configuration can be coupled into an antiferromagnetic singlet ground state. The spin-polarized singlet state derived from this coupling was further stabilized by 1.43 kcal mol^{-1} with respect to the $^7A_2$ configuration. After projection onto the proper spin eigenstate,[18] the computed value of $-2J$ is 113.3 cm^{-1}, far beyond the values currently encountered for the exchange coupling parameter in dinuclear complexes of Co^{II}. The order of magnitude of the exchange coupling then becomes comparable with the spin–orbit coupling constant λ ($\lambda = -172$ cm^{-1} for the free Co^{II} ion).

Another set of low-energy states implies a low-spin ($S = {}^1/_2$) configuration for Co^{II}. The molecular state of maximal spin is then a triplet ($^3A_2$) in which the unpaired electrons are accommodated in the two highest σ-type MOs (Figure 4). This state was computed to be 12.5 kcal mol^{-1} above the ground state, and coupling between the two unpaired electrons yields a second antiferromagnetic singlet, at +9.5 kcal mol^{-1}.

Finally, we considered an electronic state characterized by delocalized bonding interaction along the metal framework. Such a state is deduced from the doublet ground state of *s*-$[Co_3Cl_2(dpa)_4]$ by accommodating the extra electron of Pd^{II} on the nonbonding (nb) σ MO (Figure 4). This yields a closed-shell state with σ_{nb} as the HOMO that displays a four-electron/three-center bond. Surprisingly, this state lies as much as 36 kcal mol^{-1} above the ground state (Figure 4). The reason for this destabilization should be looked for in the unbalanced Co←Pd→Co charge transfer implied by the lack of contribution from Pd to the σ_{nb} MO (Figure 3). The diamagnetic state therefore entails a formal oxidation state of III for Pd, with concomitant reduction of the neighboring Co atoms. Such an unfavorable reorganization of the atomic electron density obviously offsets the benefit of delocalized bonding.

In conclusion, we have prepared and characterized an unprecedented metal-chain complex with heterometallic Co/Pd core. Both the crystal structure and the magnetic measurements suggest that the ground state results from coupling between the Co^{II} ions, both in high-spin configuration. Density functional calculations confirm this assignment and predict a relatively large isotropic exchange interaction. However, the orbital degeneracy characteristic of high-spin Co^{II} requires that spin–orbit coupling terms and anisotropic corrections are taken into account. The electronic ground state of $[Co_2PdCl_2(dpa)_4]$ and the magnetic behavior of Co^{II} in this complex are therefore strongly at variance with those observed in the tricobalt homologue. This suggests that the accommodation of the additional electron provided by the central palladium ion in the σ nonbonding MO centered on the terminal cobalt ions offsets the advantage of a delocalized bond along the metal chain. The insertion of one or several heterocenter(s) in a string of metal atoms of definite length could therefore provide a new way of tuning its magnetic and conducting properties.

Experimental Section

Synthesis: Full experimental details and analytical data can be found in the Supporting Information

Crystal data for **1**: $Co_2PdC_{44}H_{42}N_{12}Cl_2O$, $M = 1050.06$, monoclinic space group $P2_1/c$, $a = 16.0656(9)$, $b = 15.7468(8)$, $c = 17.0694(9)$ Å, $\alpha = 90$, $\beta = 97.895(1)$, $\gamma = 90°$, $V = 4277.3(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.631$ mg m^{-3}, $R_1 = 0.0297$, $wR_2 = 0.0688$. Details on data collection are given in the Supporting Information. CCDC 623473 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT/B3LYP calculations: Details of the used atomic basis sets can be found in the Supporting Information.

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[1] *Extended Linear Chain Compounds*, *Vols. 1–3* (Ed.: J. S. Miller), Plenum, New-York, **1982**.
[2] a) D. H. Chae, J. F. Berry, F. A. Cotton, C. A. Murillo, Z. Yao, *Nano Lett.* **2006**, *6*, 165; b) I.-W. P. Chen, M.-D. Fu, W.-H. Tseng, J.-Y. Yu, S.-H. Wu, C.-J. Ku, C.-h. Chen, S. M. Peng, *Angew. Chem.* **2006**, *118*, 5946; *Angew. Chem. Int. Ed.* **2006**, *45*, 5814; Erratum: I.-W. P. Chen, M.-D. Fu, W.-H. Tseng, J.-Y. Yu, S.-H. Wu, C.-J. Ku, C.-h. Chen, S. M. Peng, *Angew. Chem.* **2006**, *118*, 6390; *Angew. Chem. Int. Ed.* **2006**, *45*, 6244.
[3] J. F. Berry in *Multiple Bonds between Metal Atoms*, 3rd ed. (Eds.: F. A. Cotton, C. A. Murillo, R. A. Walton), Springer Science, New York, **2005**.
[4] J. K. Bera, K. R. Dunbar, *Angew. Chem.* **2002**, *114*, 4633; *Angew. Chem. Int. Ed.* **2002**, *41*, 4453.
[5] a) W. Zhang, A. Behrens, J. Gätjens, M. Ebel, X. Wu, D. Rehder, *Inorg. Chem.* **2004**, *43*, 3020; b) Z.-X. Zhang, Y. Li, K.-C. Li, W.-D. Song, Q.-S. Li, H.-P. Xiong, J.-Q. Xu, L.-Y. Pan, *J. Mol. Struct.* **2006**, *791*, 117; c) N. Amir, M. Motonishi, M. Fujita, Y. Miyashita, K. Fujisawa, K. Okamoto, *Eur. J. Inorg. Chem.* **2006**, 1041.
[6] T. Tanase, R. A. Begum, *Organometallics* **2001**, *20*, 106.
[7] a) L. R. Falvello, J. Forniés, R. Garde, A. García, E. Lalinde, M. T. Moreno, A. Steiner, M. Tomás, I. Usón, *Inorg. Chem.* **2006**, *45*, 2543; b) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Montiel, M. E. Olmos, J. Pérez, *Organometallics* **2006**, *25*, 1689.
[8] a) E.-C. Yang, M.-C. Cheng, M.-S. Tsai, S.-M. Peng, *J. Chem. Soc. Chem. Commun.* **1994**, 2377; b) F. A. Cotton, L. M. Daniels, C. A. Murillo, I. Pascual, *J. Am. Chem. Soc.* **1997**, *119*, 10223.
[9] R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, K. Kirschbaum, C. A. Murillo, A. A. Pinkerton, A. J. Schultz, X. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 6226.
[10] a) O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**; b) R. Boča, *Coord. Chem. Rev.* **2004**, *248*, 757.
[11] Gaussian 03 (Revision B.05): M. J. Frisch et al., see Supporting Information
[12] P. Kiehl, M.-M. Rohmer, M. Bénard, *Inorg. Chem.* **2004**, *43*, 3151.
[13] K. Fink, C. Wang, V. Staemmler, *Inorg. Chem.* **1999**, *38*, 3847.
[14] S. M. Ostrovsky, K. Falk, J. Pelikan, D. A. Brown, Z. Tomkowicz, W. Haase, *Inorg. Chem.* **2006**, *45*, 688.
[15] H. Sakiyama, *Inorg. Chim. Acta* **2006**, *359*, 2097.
[16] a) M. J. Hossain, M. Yamasaki, M. Mikuriya, A. Kuribayashi, H. Sakiyama, *Inorg. Chem.* **2002**, *41*, 4058; b) H. Sakiyama, *J. Chem. Software* **2001**, *7*, 171.
[17] L. Noodleman, C. Y. Peng, D. A. Case, J. M. Mouesca, *Coord. Chem. Rev.* **1995**, *144*, 199.
[18] M. Mitani, H. Mori, Y. Takano, D. Yamaki, Y. Yoshioka, K. Yamaguchi, *J. Chem. Phys.* **2000**, *113*, 4035.

