Inorg. Chem. **2003**, *42*, 5804–5806

Inorganic Chemistry
Communication

The First Azide($\mu_{1,1}$)-Bridged Binuclear Cobalt(II)–Imino Nitroxide Complex with Ferromagnetic Behavior

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Received June 21, 2003

The first azide($\mu_{1,1}$)-bridged binuclear cobalt(II) complex with a chelated imino nitroxide radical, $[Co_2(immepy)_2(N_3)_4]\cdot 2EtOH$, was structurally and magnetically characterized, where immepy = 4,4,5,5-tetramethyl-2-(6′-methyl-2′-pyridyl) imidazoline-1-oxyl. Five nitrogen atoms complete the coordination sphere of the Co(II) ion, showing a distorted trigonal bipyramid geometry. Two N_3^- anions act as bridges between cobalt ions in the $\mu_{1,1}$ coordination mode, resulting in a binuclear structure with an inversion center. Magnetic studies show that ferromagnetic couplings occurred between the adjacent cobalt(II) ions through $N_3^-(\mu_{1,1})$ bridges, and antiferromagnetic couplings between the cobalt(II) ions and organic radicals.

Recent efforts in molecular magnetism have produced a plethora of fascinating molecule-based materials.[1] In the field, the binuclear complexes of transition metals are one of the more extensively studied systems.[2] The azide anion is a versatile ligand which can link to transition metal atoms with different coordination modes, thus allowing for the assembly of binuclear complexes with a wide range of magnetic behavior. When the azide group acts as a bridging ligand with end-on coordination, the resulting binuclear complexes usually show ferromagnetic behavior. In contrast, when it is coordinated in an end-to-end fashion, antiferromagnetic coupling results.[3] On the other hand, these systems provide excellent examples on which the development of molecular magnetism of suitable theoretical models affords a better understanding of the exchange interaction in lattices. Since ferromagnetism in molecular complexes is much less frequent than antiferromagnetism, the ferromagnetic end-on azide-bridged transition metal complexes are especially interesting. As a result, extensive magnetostructural work has been carried out on azido-bridged binuclear copper(II),[4] manganese(II),[5] and nickel(II)[6] complexes, and their DFT calculation results have been reported.[7] Few studies of binuclear cobalt(II) complex with azide($\mu_{1,1}$) bridges were reported so far, although the honeycomblike layer cobalt(II) complex[8] with azide($\mu_{1,1}$) bridged and one-dimensional chain cobalt(II) complex[9] with $\mu_{1,1}$-N_3 and $\mu_{1,3}$-N_3 alternate bridges have been reported. Additionally, the binuclear Co(II) derivative of *Carcinus maenas* hemocyanin Co(II)−N_3−Hc has also been studied;[10] noteworthily, their structures were not determined by single-crystal X-ray diffraction. In this

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10.1021/ic034710s CCC: $25.00

contribution, we report the synthesis, structure, and magnetic properties of an azide($\mu_{1,1}$)-bridged binuclear Co(II) complex with a chelated imino nitroxide radical, $[Co_2(immepy)_2(N_3)_4]\cdot 2EtOH$. To the best of our knowledge, this is the only crystallographically characterized example of a binuclear cobalt(II) complex with an azide($\mu_{1,1}$) bridge.

4,4,5,5-Tetramethyl-2-(6′-methyl-2′-pyridyl)imidazolin-1-oxyl radical (immepy) was prepared by the literature method.[11,12] The title complex was prepared as follows: Solid NaN_3 was added to the solution of immepy and $Co(ClO_4)_2\cdot 6H_2O$ in ethanol. The mixture solution was stirred at 60°C for 5 h, blue precipitates formed, and then the precipitates were removed by filtration. The filtrate slowly evaporated at room temperature in the dark for a month, and the blue single crystal suitable for X-ray analysis was obtained. Anal. Calcd for $C_{30}H_{48}Co_2N_{18}O_4$: C, 42.77; H, 5.75; N, 29.95. Found: C, 42.85; H, 5.63; N, 29.85. The IR spectrum displays two strong bands at 2067 and 2047 cm^{-1}, respectively, which are the characteristic $\nu(N_3^-)$ band. The strong band observed at 1372 cm^{-1} is the $\nu(N-O)$ band.

Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Vario EL III elemental analyzer. The infrared spectrum was taken on an AVATAR FT-IR spectrophotometer in the 4000−400 cm^{-1} region, using KBr pellets. Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 diffractometer equipped with graphite-monchromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by the $\varphi-\omega$ scan technique in the range $2.42° \le \theta \le 25.02°$ with a total of 3544 reflections collected including 1913 independent reflections ($R_{int} = 0.1646$). Temperature dependent magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

The structure[13] of the title complex is shown in Figure 1. Five nitrogen atoms complete the coordination sphere of the Co(II) ion, showing a distorted trigonal bipyramid geometry, of which three nitrogen atoms, N2, N4A, and N7, construct the trigonal plane, and two, N(1) and N(4), occupy the axial positions. The distortion along the axial direction is demonstrated by the N1−Co1−N4 angle of 171.7(2)°. The bond lengths of Co−N in the plane (Co1−N2, Co1−N4A, and Co1−N7, equal to 2.062(7), 2.049(8), and 2.029 Å, respectively) are shorter than those of Co−N (Co1−N1 = 2.235 Å and Co1−N4 = 2.209 Å) down the axial direction. Two N_3^- anions act as bridges between cobalt ions in the $\mu_{1,1}$ coordination mode, resulting in a binuclear structure with an inversion center. The Co−Co distance of 3.344 Å is essentially too long to exist in a metal−metal bond.[14] The angle of Co1−N4−Co1A is 103.4(3)°, which falls in the range 100−107°, corresponding to an M−N−M bond angle (M = Cu, Ni, and Mn(II)).[3g] The dihedral angle between the imino nitroxide fragment and the pyridine ring of the radical is 8.2(10)°, which is consistent with that of the corresponding $\{[NiCl(immepy)]_2(\mu\text{-}Cl)_2\}$.[15]

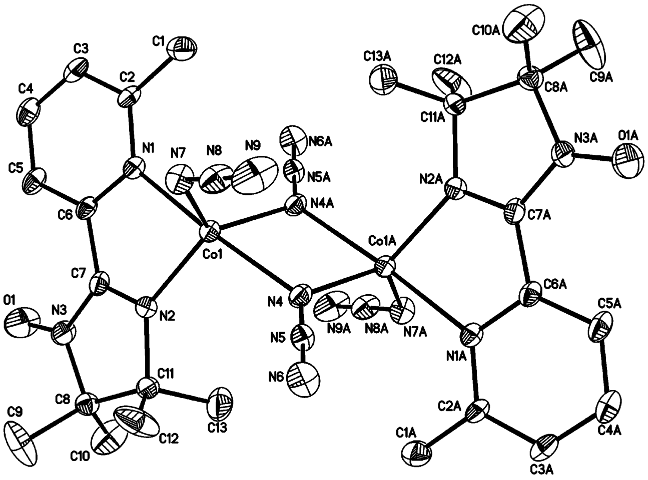

Figure 1. ORTEP drawing of the complex. Thermal ellipsoids are drawn at the 30% probability level. The uncoordinated EtOH molecules are omitted for clarity.

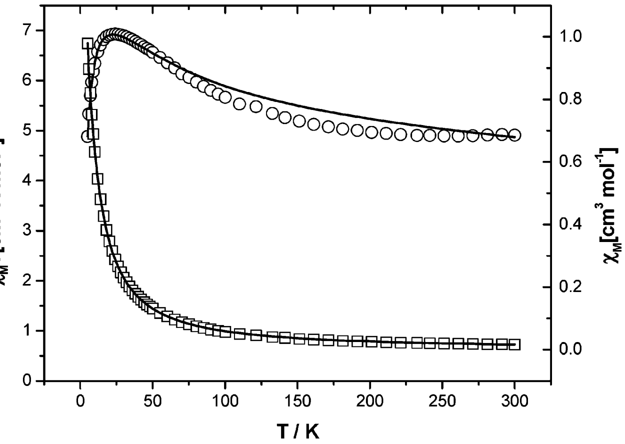

Figure 2. The plots of $\chi_m T$ and χ_m versus T for the complex, the solid line showing the best fit to the values.

The variable temperature magnetic susceptibility data for a crystalline sample of the complex was measured on SQUID susceptometer over the temperature range 5−300 K with an applied field of 10000 G. The plots of $\chi_M T$ and χ_M vs T are shown in Figure 2. The $\chi_M T$ value of 4.96 cm^3 K mol^{-1} was observed at room temperature, which is larger than the expected spin-only value of 4.50 cm^3 K mol^{-1} for non-interaction of two $S = {}^3/_2$ spins of Co(II), and two $S = {}^1/_2$ spins of radicals. With decreasing the temperature, the $\chi_M T$ value increases gradually to reach a maximum value of 7.01 cm^3 K mol^{-1} at 24 K, and decreases sharply with the

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(13) Crystal data for the complex: $C_{30}H_{48}Co_2N_{18}O_4$, $M_w = 842.72$, triclinic, space group $P\bar{1}$, $a = 9.91(3)$ Å, $b = 10.17(3)$ Å, $c = 11.12(3)$ Å, $\alpha = 87.19(6)°$, $\beta = 72.47(5)°$, $\gamma = 85.39(6)°$, $V = 1065(5)$ Å^3, $Z = 1$. $F(000) = 440$, $\mu = 0.834$ mm^{-1}, $\lambda = 0.71073$ Å. $T = 293(2)$ K, $2\theta_{max} = 50.04°$. $R_1 = 0.0864$ for 1913 reflections with $I > 2\sigma(I)$. GOF = 1.077, residual electron density between −0.623 and 0.780 e Å^{-3}. CCDC reference number 210728. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cm.ac.uk).

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temperature further lowered. This magnetic behavior indicates the presence of ferromagnetic interactions in the complex.

On account of the distorted trigonal bipyramid geometry of the Co center and ${}^4A_2'$ ground state with no angular momentum, the magnetic data were fit by eq 1 derived from the approximate model[16] previously reported:

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\frac{A}{B} \qquad (1)$$

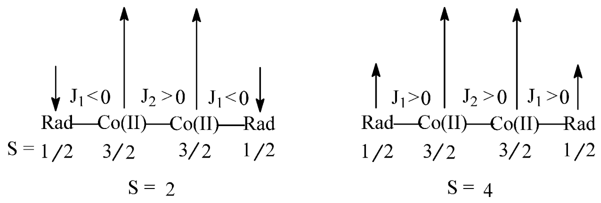
$$\begin{aligned} A = {} & 184 \exp[(6J_1 + 4J_2)/kT] + 84 \exp[6J_1/kT] + \\ & 30 \exp[(6J_1 - 3J_2)/kT] + 6 \exp[(6J_1 - 5J_2)/kT] + \\ & 168 \exp[(4J_1 + 2J_2)/kT] + 60 \exp[(4J_1 - J_2)/kT] + \\ & 12 \exp[(4J_1 - 3J_2)/kT] + 30 \exp[(2J_1 + J_2)/kT] + \\ & 6 \exp[(2J_1 - 2J_2)/kT] \end{aligned}$$

$$\begin{aligned} B = {} & 9 \exp[(6J_1 + 4J_2)/kT] + 7 \exp[6J_1/kT] + \\ & 5 \exp[(6J_1 - 3J_2)/kT] + 3 \exp[(6J_1 - 5J_2)/kT] + \\ & \exp[(6J_1 - 6J_2)/kT] + 14 \exp[(4J_1 + 2J_2)/kT] + \\ & 10 \exp[(4J_1 - J_2)/kT] + 6 \exp[(4J_1 - 3J_2)/kT] + \\ & 5 \exp[(2J_1 + J_2)/kT] + 3 \exp[(2J_1 - J_2)/kT] + \\ & \exp[(2J_1 - 2J_2)/kT] \end{aligned}$$

where J_1 corresponds to the coupling between the cobalt(II) ion and radical and J_2 stands for coupling between the Co−R units fabricated through N_3^- bridges.

The least-squares analysis of magnetic susceptibility data led to $J_1 = -15.4$ cm^{-1}, $J_2 = 17.7$ cm^{-1}, $g = 2.08$, and $R = 4.32 \times 10^{-5}$ (the agreement factor defined as $R = \sum(\chi_{obsd} - \chi_{calcd})^2/(\chi_{obsd})^2$). The $J_1 < 0$ indicates antiferromagnetic coupling interaction between Co(II) ion and radical. The parameter $J_2 > 0$ suggests ferromagnetic interaction between the Co−R units, which may be attributed to the polarization effect of azide($\mu_{1,1}$) bridges and is consistent with the magnetic properties in the end-on azide-bridged transition metal complexes reported previously. The g value is lower than the value for normal Co complexes, but is similar to that of the Co complex with similar geometry in the literature.[17]

Scheme 1



To further support the nature of the interaction provided by the temperature dependence of magnetization, the field dependence of the magnetization for the complex was measured in 0−5 T at 5 K. The experimental values of M for the title compound were compared to those calculated by the Brillouin function corresponding to the $S = 4$ and $S = 2$ spin states (Scheme 1), respectively. The plots of M vs H are shown in Figure 3, and the corresponding experimental values (○) are displayed between the two solid lines that correspond to the (A) $S = 4$ and (B) $S = 2$ states. However, the experimental values are closer to those of the $S = 2$ state and far from the $S = 4$ state, which confirms that the ground state of $S = 2$ results from ferromagnetic interactions between the units consisting of Co ion and radical and antiferromagnetic coupling within the unit.

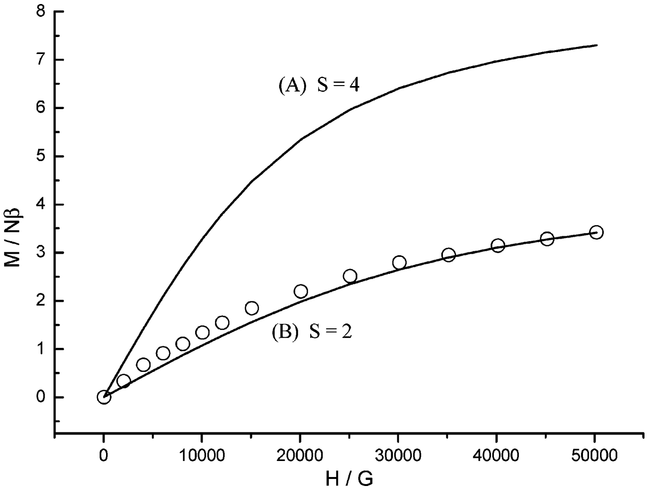


Figure 3. Experimental field dependence of the magnetization for the compound (○) and Brillouin curves based on $S = 2$ (solid B) and $S = 4$ (solid A) spin states.

In conclusion, an azide-bridged binuclear cobalt(II) complex simultaneously containing immepy radical was successfully isolated, and structurally and magnetically characterized. To our knowledge, the complex is the first example of a binuclear Co(II) complex bridged by $\mu_{1,1}$-azide. Magnetic study revealed ferromagnetic coupling between the units of Co(II) ion and radical, and antiferromagnetic interaction within the unit.

Acknowledgment. This work was supported by the NNSF of China (20171025 and 90101028).

Supporting Information Available: The tables of selected bond lengths and angles for the complex and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034710S

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