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Magnetic Properties of the Ternary Complex Bis[(adenosine 5′-triphosphato)(2,2′-bipyridine)copper(II)] Tetrahydrate

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The first crystal structure determination of a metal–ATP complex was reported recently,[1] showing that, in bis[(adenosine 5′-triphosphato)(2,2′-bipyridine)zinc(II)], dimeric molecules are present in which the two zinc atoms were held together by two –O–P–O– bridges from the α-phosphates of two ATP moieties. Both zinc atoms show a 5 + 1 coordination environment, formed by two oxygen atoms from two different α-phosphate groups, one β-oxygen atom, and the two nitrogen atoms of the bipyridyl group. Since the copper complex was reported to have a very similar X-ray powder pattern,[1] showing that the complex presumably has a coordination geometry similar to that of the zinc derivative,[2] we decided to obtain accurate magnetic susceptibility data on bis[(adenosine 5′-triphosphato)(2,2′-bipyridine)copper(II)], [Cu(ATP)(bpy]$_2$, in order to ascertain the extent of magnetic coupling between the two metal ions determined by the bridging –O–P–O– moieties.

Results and Discussion

EPR spectra of polycrystalline powders of [Cu(ATP)(bpy)]$_2$ recorded at room temperature and 4.2 K are similar to each other and are in agreement with the presence of a dimeric species, as shown by the $\Delta M = 2$ transition resolved at half-field (see Figure 1). The spectra in the $\Delta M = 1$ region are not easily interpreted, because the lines largely overlap each other. Tentatively the values $g_\parallel = 2.32$ and $g_\perp = 2.09$ can be assigned, assuming that the zero-field splitting is smaller than the experimental line width. Since the metal–metal distance in the zinc complex is 489 nm, the dipolar contribution to the zero-field splitting requires a D value of the order of 200 G, which is compatible with the spectrum experimentally observed. Room-temperature Q-band spectra agree with this analysis, showing a broad feature at $g_\parallel = 2.32$ and another one at $g_\perp = 2.09$. Attempts were made also to measure frozen-solution spectra, but these are dominated by the signal of a monomeric species with $g_\parallel = 2.30$, $g_\perp = 2.06$, and $A_\parallel = 183 \times 10^{-4}$ cm^{-1}.

Pairs of interacting copper ions exhibit a singlet and a triplet electronic state, separated by an energy of $-2J$. The fact that the EPR spectra of [Cu(ATP)(bpy)]$_2$ can be obtained at 4.2 K shows either that the triplet is the ground state or that its separation from the ground singlet is on the order of several wavenumbers. We therefore measured the magnetic susceptibility in the range 1.2–4.2 K in order to have an accurate measurement of the magnetic exchange coupling between the two metal ions.

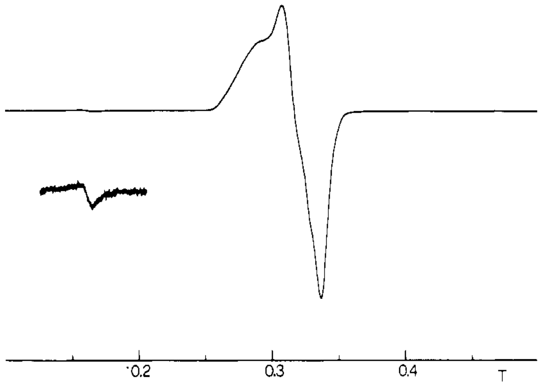

Figure 1. Polycrystalline powder EPR spectrum of [Cu(ATP)(bpy)]$_2$ at room temperature and X-band frequency.

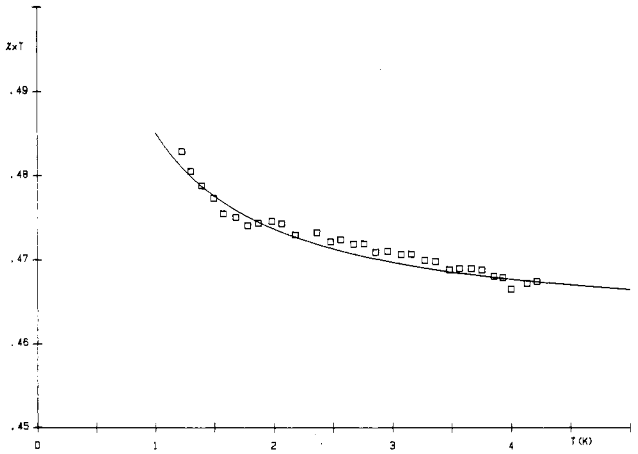

Figure 2. χT vs. T plot of experimental data (data points). Solid line is the curve calculated with the best fit parameters.

In Figure 2 the experimental points are shown in a χT vs. T plot, since this function is known to be a sensitive one in the case of weakly coupled systems.[3] The value of χT at 4.2 K is 4.674×10^{-1} emu K, corresponding to a magnetic moment of $\mu = 1.93$ μ_B, and it increases smoothly with decreasing temperature until, at 1.2 K, $\chi T = 4.828 \times 10^{-1}$ emu K and $\mu = 1.96$ μ_B per copper atom.

The experimental χT points were fit to the Bleaney–Bowers equation,[4] by using the spin Hamiltonian in the form $H = -2J\vec{S}_1\cdot\vec{S}_2$. The best fit curve, shown in Figure 2, was obtained by a least-squares procedure, yielding $g = 2.218$ (1) and $2J = 0.15$ cm^{-1} (0.22 K). The factor $R = (\sum_i(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2T_i^2/\sum_i(\chi_i^{\text{obsd}}T_i)^2)^{1/2}$ is found to be 1.98×10^{-5}, and the linear correlation coefficient between the parameters is -0.9401.

The isotropic constant is very small and positive, showing that the coupling between the two metal ions is ferromagnetic in nature. The fitted value should be reliable, because the zero-field splitting of the triplet state, observed in the EPR spectra, is much smaller than J.

The observed small coupling etween the two copper ions is easily understood on the basis of the structural data of the zinc analogue.[1] Although one oxygen atom of the bridging –O–P–O– moiety occupies an equatorial position in the coordination environment of one copper ion, thus giving a good overlap with the $x^2 - y^2$ magnetic orbital, the second oxygen occupies an axial position in the coordination environment of the second copper ion, thus giving only a poor overlap to the magnetic orbital. Further, it is known that –O–P–O– bridges are not very effective in transmitting the magnetic coupling: in a series of polymeric metal phosphinates the largest observed constant was only a few wavenumbers,[5] and for a copper(II) complex with uridine 5′-monophosphate a value of 10.8 cm^{-1} was observed.[6]

The sign of the coupling constant is surprising, since for long distances an antiferromagnetic coupling has been more often found

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to be operative.[7] However, this result can be rationalized considering that the fraction of unpaired electron delocalized from one copper atom on the oxygen atom occupying an axial position of the other copper ion is in an orbital orthogonal to the $x^2 - y^2$ magnetic orbital of the latter. This situation is analogous to that seen in $Cu(hfac)_2TEMPOL$[8] (hfac = hexafluoroacetylactonato, TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy) and in $Cu(pacTEMPOL)_2$[9] (pacTEMPOL = bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato) where the unpaired electron on the radical is in an orbital similarly oriented with respect to the copper magnetic orbital: in both cases the coupling was reported to be ferromagnetic.

Experimental Section

The title compound was kindly supplied by Prof. P. Orioli, University of Firenze.

The EPR spectra were recorded with a Bruker ER200 spectrometer, equipped with an Oxford Instruments continuous-flow ESR10 cryostat. Q-Band spectra were recorded at room temperature on a Varian E9 spectrometer. The magnetic susceptibilities were measured by an ac mutual-inductance technique at nearly zero field.[10] The sample is immersed in liquid helium, and the temperature is measured by means of a germanium-resistance thermometer calibrated against the vapor pressure of He. Each data point is calibrated by measuring against CMN.

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Registry No. $[Cu(ATP)(bpy)]_2$, 97373-98-3.

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Coordination Chemistry of Samarium(II). X-ray Crystal Structures of $SmI_2(NCCMe_3)_2$ and $SmI_2[O(CH_2CH_2OMe)_2]_2$. The First Example of a Bent M—N≡C Structure

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Oxygen- and nitrogen-donor ligands are ubiquitous in trivalent lanthanide metal chemistry, and numerous structurally characterized compounds that incorporate these ligand types are known.[2] In contrast, very few soluble, well-characterized, compounds of the lanthanide elements in the divalent state have been reported [only three for Sm(II): the $Sm(C_5Me_5)_2$ derivatives[3]]. Except for a few compounds incorporating the sterically demanding ligand $N(SiMe_3)_2$,[4] we are unaware of structurally characterized coordination compounds of any of the divalent lanthanide metal ions that contain simple oxygen- and nitrogen-donor ligands. Herein, we report the synthesis and X-ray crystal structures of two Sm(II) derivatives: $SmI_2(NCCMe_3)_2$ (**1**) and $SmI_2[O(CH_2CH_2OMe)_2]_2$ (**2**). As detailed below, these present several interesting structural features, including a unique bent M—N≡C structure for **1**. The latter is of particular interest in view of the isoelectronic relationship between R—C≡N and N≡N. In addition, the preparation and characterization of soluble compounds are important for the elaboration of the chemistry of divalent lanthanide metal ions. We also note here that SmI_2 in oxygen-donor solvents has been used extensively as a reducing agent in organic chemistry,[5] and **1** and **2** represent the first well-characterized derivatives of SmI_2.

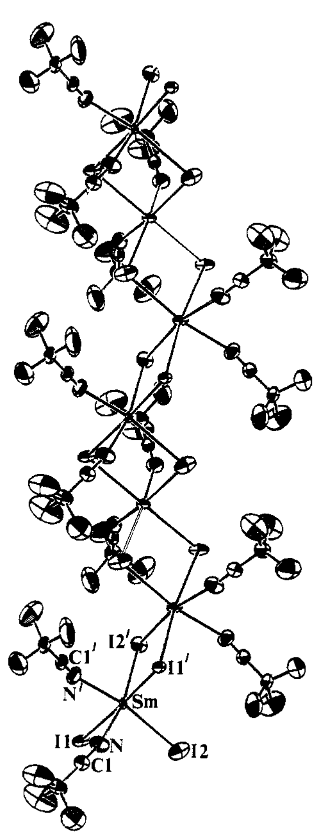

Figure 1. ORTEP drawing of **1**.

Results and Discussion

1 was obtained as dark green crystals by the reaction of SmI_2 with Me_3CCN at 25 °C. An X-ray crystal structure of **1** revealed the geometry around each samarium to be a distorted octahedron, the ligating atoms being the two nitrogens and the four bridging iodides. All the iodide ions are bridging, and this results in infinite chains of repeating unit $SmI_2(NCCMe_3)_2$, with an average Sm–I distance of 3.242 (1) Å (Figure 1). The samarium lies on a twofold axis that generates a complete monomeric unit; in addition, a twofold axis passes through both unique iodide ions, thus generating the bridging iodide polymeric structure of **1**. The two nitrile ligands have a cis configuration with Sm–N distances of 2.596 (8) Å.

The most remarkable structural feature of **1** is the Sm—N≡C angle of 151.3 (6)°.[6] Crystal structures of nitrile adducts of the actinides,[7] the transition metals,[8] and the main-group elements[9]

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