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The Crystal Structure of [La(NO₃)₆{Cu(2,2'-bipy)₂}₂][La(NO₃)₆Cu(2,2'-bipy)₂]•CH₃CN with the Most Profuse Modes of Nitrate Coordination

The title compound [La(NO₃)₆{Cu(2,2'-bipy)₂}₂][La(NO₃)₆Cu(2,2'-bipy)₂]•CH₃CN was synthesized, the crystal and molecular structures were determined at room temperature. The complex formed monoclinic crystals, space group *P2₁/n*(No.14), *a* = 10.354 (3) Å, *b* = 23.440 (9) Å, *c* = 32.817 (9) Å, β = 90.39 (2)°, *Z* = 4. The crystal structure consisted of a discrete [La(NO₃)₆{Cu(2,2'-bipy)₂}₂] cation and [La(NO₃)₆Cu(2,2'-bipy)₂] anion and a non-coordinated CH₃CN molecule. Each La(III) ion was 12-coordinate with twelve oxygen atoms from six chelating nitrate ligands. There were four modes of nitrate coordination and the coordination geometry of all three copper ions was different in the crystal structure.

Keywords: crystal structure, nitrate coordination

Introduction

There was much current interest in the syntheses and structures of mixed copper-lanthanide complexes. This work was chiefly motivated by (I) their use as the precursor complexes of the superconducting materials in MOCVD; (II) the unusual magnetic interactions between d- and f-block elements. Many advances in this general area were focused on studies of the properties of bridging ligands such as dbm (dibenzoyl methane) (MIELE, P. et al.), alkoxides and β -diketonates (BIDELL, W. et al.), amino alcohols (CHEN, L. et al.), 2-hydroxypyridine or its derivatives (BLAKE, A. J. et al.) etc. In contrast, d- and f-block metals bridged by only nitrate groups has been unprecedented, although nitrate group was a very common bridging ligand. And note in passing that there was also a growing interest in materials in which metal ions were linked through oxoanions such as phosphate groups (BUJOLI, B. et al. and MARCOS, M. D. et al.). On the other hand, it was usually difficult to isolate these Cu-Ln (lanthanide) complexes from solution due to their high solubility and tendency to form oily material in common organic solvents (WANG, S. et al.), thus making the investigation of their syntheses, structures, physical and chemical properties difficult. We therefore explored the syntheses of Cu-La complexes with La(NO₃)₃ and Cu(NO₃)₂ and other simple, non-bridging ligands in the various solutions and reported herein a novel complex of [La(NO₃)₆{Cu(2,2'-bipy)₂}₂][La(NO₃)₆Cu(2,2'-bipy)₂]•CH₃CN (I) with the most profuse modes of nitrate coordination and three different copper coordination structures.

Experimental

Preparation of the crystal

To a mixture of Cu(NO₃)₂•3H₂O (241.63 mg, 0.75 mmol) and La(NO₃)₃•6H₂O (357.35 mg, 0.30 mmol) in 30 ml CH₃CN was added 1.5 mmol of 2,2'-bipyridine of 15 ml CH₃CN. Dark

blue solution was obtained and allowed to crystallize by slow evaporation, producing X-ray quality deep blue crystals after several days. Elemental analysis was found: Cu, 8.51; C, 35.25; H, 2.35; N, 16.38; Calc. For (I): Cu, 8.82; C, 33.99; H, 2.35; N, 15.98.

X-ray investigation

Crystal data: $[\text{La}(\text{NO}_3)_6\{\text{Cu}(2,2'\text{-bipy})_2\}_2][\text{La}(\text{NO}_3)_6\text{Cu}(2,2'\text{-bipy})_2]\bullet\text{CH}_3\text{CN}$, Mw = 2190.68, monoclinic, Space group: $P2_1/n(\text{No.}14)$, $a = 10.354(3) \text{ \AA}$, $b = 23.440(9) \text{ \AA}$, $c = 32.817(9) \text{ \AA}$, $\beta = 90.39(2)^\circ$, $Z = 4$, $V = 7964.7 \text{ \AA}^3$, $F(000) = 4348$, $D_c = 1.83 \text{ g/cm}^3$, $T = 296 \text{ K}$, $\mu(\text{Mo-K}\alpha) = 19.5 \text{ cm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$. A crystal of approximate dimensions $0.25 \times 0.20 \times 0.10 \text{ mm}^3$ was mounted on a Rigaku AFC5R diffractometer, using graphite monochromatized Mo-K α radiation. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $8^\circ < \theta < 27.5^\circ$, measured by the computer controlled diagonal slit method of centering. Three reflections were monitored periodically as a check for crystal decomposition and movements. Scan mode of ω - 2θ and maximum 2θ value being 50° were used to collect intensity data. A total of 15263 reflections were collected, of which 15263 were unique, and 3190 had $I > 3\sigma(I)$ for 538 parameters. The data were corrected for Lorentz and polarization effects, and absorption was corrected empirically for three reflections. The structure was solved by direct methods and refined by full matrix least-square calculation. La atoms were located in the E map, the remaining atoms were located in succeeding difference Fourier syntheses and H atoms further included as fixed contribution to the structure factor. All calculations were performed on a COMPAQ computer using MoLEN/PC program (MOLEN). A weighting scheme with $w = 1/[\sigma^2(F\sigma)^2 + (0.020Fo)^2 + 1.000]$ was used. Neutral atomic scattering factors were taken from the International Tables for X-ray Crystallography (CROMER, D. T. et al.). At final convergence, $R = 0.072$, $R_w = 0.080$, $\text{GOF} = 1.36$, maximum shift/e.s.d = 0.03. The minimum and maximum peaks in final difference Fourier map were $0.22(19) \text{ e/ \AA}^3$ and $0.99(19) \text{ e/ \AA}^3$, respectively.

Selected atomic coordinates and equivalent isotropic parameters were given in Table 1. Selected bond lengths and angles were given in Table 2 and 3, respectively.

Results and discussion

The molecule structure of the title complex consisted of discrete $[\text{La}(\text{NO}_3)_6\{\text{Cu}(2,2'\text{-bipy})_2\}_2]^+$ cation and $[\text{La}(\text{NO}_3)_6\text{Cu}(2,2'\text{-bipy})_2]^-$ anion and a non-coordinated CH_3CN molecule, see Fig. 1 and 2.

It was worth noting that each Cu had different coordination geometry. Cu(3) had a trigonal bipyramidal [the geometric τ value was 0.55 (ADDISON, A. W. et al.)] coordination with CuN_4O coordination sphere. The coordination geometry around Cu(2) was at least five-coordinate, and that of a distorted square pyramid (the τ value was 0.41). In addition, the O(133) atom of the coordinated nitrate was involved at a potentially bonding distance of $2.84(2) \text{ \AA}$, on the same side of the Cu, N(21)-N(24) plane as O(131), to give an unsymmetrical bidentate coordinating nitrate group which could also be found in the structure of $[\text{Cu}(\text{bipy})_2(\text{ONO}_2)][\text{NO}_3]\text{H}_2\text{O}$ (Cu-O(NO_3) bond lengths were 2.301 \AA and 2.832 \AA (FEREDAY, R. J. et al.)). In the complex $\{\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3\}$ (CASTRO et al.), it was also found that the weak coordinated Cu-O(ClO_4) distance had reached up to $2.97(2) \text{ \AA}$. Furthermore, the $[\text{Cu}(2)\text{-O}(133)]\text{-}[\text{Cu}(2)\text{-O}(131)]$ difference of 0.38 \AA was much less than that previously suggested (ADDISON, C. E. et al.) as the limit for an unsymmetrically coordinated bidentate nitrate group (0.7 \AA). These reasonably allowed us to conclude that

geometry around Cu(2) can be considered as a six-coordinate, asymmetrical cis-distorted bicapped square pyramidal coordination (FEREDAY, R. J. et al.) with a CuN4OO* structure. Also, one distant oxygen atom (O(153)) completed a 4+1* Cu(1) coordination and Cu(1) was in square pyramidal environment ($\tau = 0.14$).

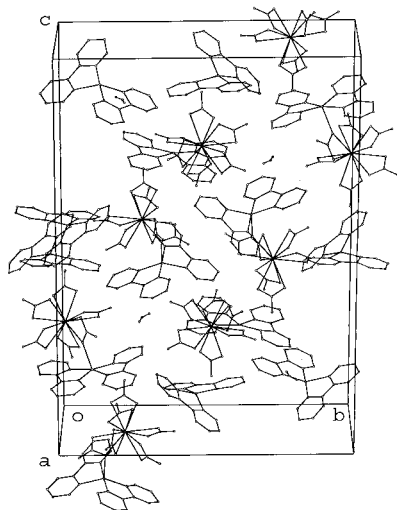


Fig. 1: The crystal structure of the title compound.

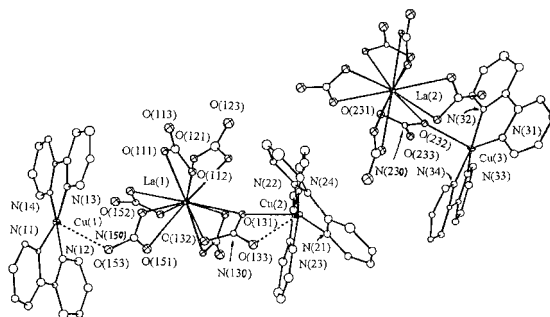


Fig. 2: The molecular structure of the title compound.

Each of the two La(III) ions was 12-coordinate with twelve oxygen atoms from six chelating nitrate ligands. The averaged La-O bond lengths 2.673 Å was in agreement with the value of 2.655 Å found in the $[\text{L.H}_3^+\text{O}][\text{La}(\text{NO}_3)_6]$ (TANG, Y. et al.). A rough estimate of the cationic distortions was furnished by the extensive equation $\Delta = (1/12)\Sigma((\text{R}_i - \text{R})/\text{R})^2$ based on the literature equation (BROWN, I. D. et al.), R_i being the individual bond length and R the average bond length. The calculated values, $\Delta(\text{La}(1)) = 0.020\%$ and $\Delta(\text{La}(2)) = 0.014\%$, were relatively higher than that found in the $[\text{L.H}_3^+\text{O}][\text{La}(\text{NO}_3)_6]$ ($\Delta(\text{La}) = 0.004\%$), a result which was in accord with the individual coordination environment.

There were four different coordination modes of nitrate ligands in the title complex. One was the simple bidentate nitrate. The nitrate group only coordinated to La(III) through two oxygen atoms. The second mode was the bridging (bidentate, unidentate) nitrate N(150)-two oxygen atoms (O(151) and O(152)) of the nitrate coordinated to La(1), while the other oxygen atom (O(153)) coordinated to Cu(1). The interaction between Cu(1) and O(153), although weak, could take into account the fact that the distance of N(150)-O(153) was 1.29 Å, slightly longer than that of N(150)-O(151) (1.19(3) Å) and N(150)-O(152) (1.24(3) Å). The third mode was the bridging (bidentate, unidentate) nitrate (N(230))-the nitrate ligand spanned La(2) and Cu(3) with one oxygen atom (O(232)). The other oxygen atom (O(231)) was only coordinated to La(2). The fourth unusual mode was the bridging (bidentate, bidentate) nitrate (N(130))-the nitrate ligand bridged La(1) and Cu(2) with one oxygen (O(131)), the remaining two oxygen atoms (O(132) and O(133)) coordinated to the La(1) and Cu(2), respectively. These various bridging modes led to several metal-metal contacts with La(1)-Cu(1) 5.67, La(1)-Cu(2) 5.03, and La(2)-Cu(3) 4.89 Å. Here, two copper atoms were linked by $\text{La}(\text{NO}_3)_6$ group forming a bent-chain arrangement, similar to those found in other LaCu_2 compounds (BENCINI, A. et al.). The nitrate ligand can coordinate

to metal ion in many ways. Most nitrate complexes contained only one or two coordination modes; it was very rare to have more than two nitrate modes within one compound. As far as we were aware, only two complexes, $[\{\text{Ph}_2\text{Te}(\text{NO}_3)_2\text{O}\}_2\text{O}]_2\text{-Ph}_2\text{Te}(\text{NO}_3)(\text{OH})$ (ALCOCK, N. W. et al.) and $[\text{Nd}(\text{H}_3\text{dha}_3\text{tren})(\text{NO}_3)_3]_n$ (YANG, L. W. et al.) had three nitrate modes. The structure of the title complex was the first example that contained four distinct nitrate modes in one crystal structure.

In conclusion, it was seen that the nitrate group could be used as a bridging ligand to form d-f block bimetallic complexes. We can envisage a wide range of compounds with this ligand system. Although we cannot predict or control the likely product of any individual reaction, we can produce a series of compounds with differing Cu:Ln ratios, with different bridging modes of the ligand and with different partial arrangements of the metals, if La(III) is replaced by other trivalent or divalent lanthanide. This type of complexes may prove valuable in the study of 3d-4f metal ion interaction.

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