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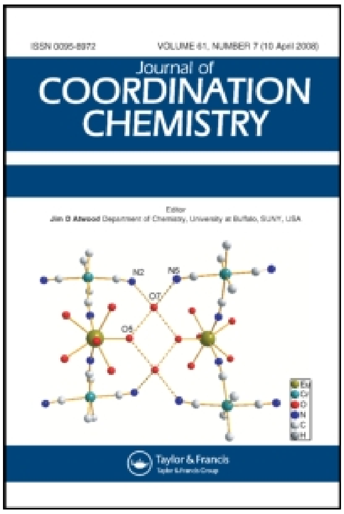

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and properties of a new complex constructed from coordinated Dy(III) unit and the polyanion $[SiMo_{12}O_{40}]^{4-}$: $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}]\cdot 2NMP$

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To cite this Article Wang, Jingping , Han, Qiuxia and Niu, Jingyang(2004) 'Synthesis, crystal structure and properties of a new complex constructed from coordinated Dy(III) unit and the polyanion $[SiMo_{12}O_{40}]^{4-}$: $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}]\cdot 2NMP$', Journal of Coordination Chemistry, 57: 1, 33 — 40
To link to this Article: DOI: 10.1080/00958970310001648199
URL: http://dx.doi.org/10.1080/00958970310001648199

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J. Coord. Chem., Vol. 57, No. 1, 10 January 2004, pp. 33–40

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A NEW COMPLEX CONSTRUCTED FROM COORDINATED Dy(III) UNIT AND THE POLYANION $[SiMo_{12}O_{40}]^{4-}$: $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$

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(Received 10 April 2003; Revised 14 July 2003; In final form 14 November 2003)

The synthesis, X-ray crystal structure, IR, UV and ESR spectra, and thermal properties of the new complex formulated $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$ (NMP = *N*-methyl-2-pyrrolidone), are reported. The crystal structure indicates that the coordinated ion combines with $[SiMo_{12}O_{40}]^{4-}$ by an electrostatic force. There are several kinds of hydrogen bonding in the complex and the crystal structure shows that the water molecules in the coordination sphere play a dual role: they coordinate to the rare earth ions on one hand and form strong hydrogen bonds on the other. The complex is strongly photosensitive under irradiation with sunlight, resulting in charge transfer by oxidation of the *N*-methyl-2-pyrrolidone and reduction of the polyoxometalate. The low-temperature ESR spectra indicate that thermal electron delocalization occurs among the Mo atoms in the complex.

Keywords: Polyoxometalates; Polyoxomolybdate; Dysprosium; Crystal structure

INTRODUCTION

Polyoxometalates are a rich class of inorganic compounds with a remarkable degree of molecular and electronic tunability. They are significant in disciplines as diverse as catalysis, medicine, and materials science [1]. Their size, shape, multi-stage redox states [2], and acentric molecular configuration are some of the remarkable molecular features of heteropolyanions with the α-Keggin structure [3], exemplified by $SiMo_{12}O_{40}^{4-}$, making them attractive precursors for the preparation of charge-transfer hybrid salts of organic–inorganic character. Many Keggin polyoxometalate-based molecular materials have been obtained by combination with organic π-electron donors, such as tetrathiafulvalene (TTF), (BET) and bis(ethylenedithio) tetrathiafulvalene (ET) [4–7], to form 1D and 2D structures. Besides organic donors, other donor

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001648199

molecules, such as decamethylferrocene, can combine with polyoxometalate acceptors [8]. In previous work, we have succeeded in taking polyoxometalates as inorganic electron acceptor components in organic–inorganic composite complexes, with the aim of examining novel structural and, in particular, photochromic and non-linear optical properties [9–11]. But compared to the reports of d-block transition metal and alkaline earth metal complexes [9–11], lanthanide complexes are less common. We have previously reported the syntheses, characterization, and crystal structures of $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ [12] and $[Sm(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ [13]. Continuing the effort to investigate this family of derivatives, we report herein the synthesis, crystal structure, and characterization of $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$.

EXPERIMENTAL

Materials

All organic solvents for synthesis and physical measurements were reagent grade and used without further purification. The $H_4SiMo_{12}O_{40} \cdot nH_2O$ was prepared by the literature method and confirmed by IR and UV spectra [14].

Physical Measurements and Analyses

C, H, and N elemental analyses were performed on a Perkin-Elmer 240C instrument. IR spectra of the sample were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the range 4000–500 cm^{-1}. UV spectra were observed in acetonitrile–water ($v:v = 2:1$) solution with an England Heλiosα spectrophotometer. Thermogravimetric analysis (TG-DTA) was performed in air on a Perkin Elmer-7 instrument with a heating rate of 10°C/min from room temperature to 600°C. The X-bond ESR spectra of the powder were recorded on a Bruker ER-200-D-SRC spectrometer at 110 K after exposure to sunshine had changed the color to dark blue.

Preparation of the Title Compound

1.5 mmol $DyCl_3$ (0.28 g 99.9% Dy_2O_3 dissolved in HCl) and $H_4SiMo_{12}O_{40} \cdot nH_2O$ (2 g, 1.0 mmol) were dissolved in 10 cm^3 aqueous solution and stirred below 90°C until some solids precipitated, followed immediately by addition of 1 cm^3 *N*-methyl-2-pyrrolidone. With vigorous stirring a solid paste appeared, which was dissolved in an acetonitrile–water mixture (2 : 1 v/v), filtered, and left to evaporate at room temperature. One or two days later, crystals suitable for X-ray diffraction were obtained; yield based on $H_4SiMo_{12}O_{40} \cdot nH_2O$ is about 70%. Anal. Calcd. for $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$ (%): C, 13.74; H, 2.31; N, 3.21. Found: C, 13.79; H, 2.43; N, 3.28.

X-ray Structure Determination

A single crystal with dimensions $0.26 \times 0.23 \times 0.20$ mm was selected for crystal-structure analysis. The data were collected at room temperature on a Rigaku

RAXIS-IV image plate area detector with Mo Kα ($\lambda = 0.7103$ Å) radiation. The crystal is monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 17.4918(6)$ Å, $b = 18.1892(4)$ Å, $c = 22.9417(7)$ Å, $\beta = 105.0190(10)^\circ$, $V = 7049.8(4)$ Å^3, $Z = 4$, $D_x = 2.471$ g cm^{-3}. A total of 22 577 reflections were collected ($2.22 < \theta < 25.00^\circ$, $-20 \leq h \leq 20$, $-21 \leq k \leq 21$, $-27 \leq l \leq 27$). The refinement converged at $R = 0.0439$ over 12 232 reflections with $I \geq 2\sigma(I)$, $wR = 0.1158$, $w^{-1} = [\sigma^2(F_o^2) + (0.0587P)^2 + 39.5643\,P]$ [where $P = (F_o^2 + 2F_c^2)/3$]. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 program [15]. The maximum and minimum residual peaks on the final difference Fourier map were 2.077 and -1.398 e Å^{-3}, respectively.

RESULTS AND DISCUSSION

X-ray Structure

The structure of the complex is shown in Fig. 1. The molecular structure of $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$ consists of an anionic Keggin $SiMo_{12}O_{40}^{4-}$ unit and a coordination cation $[Dy(NMP)_4(H_2O)_3]^{3+}$. The selected bond lengths and angles are listed in Table I. The molecular geometry of this polyanion is constrained by the fact that $SiMo_{12}O_{40}^{4-}$ is a known Keggin structure [3] formed from a central SiO_4 tetrahedron whose O atoms are part of the cage of twelve surrounding MoO_6 octahedra linked to each other by sharing corners and edges. The Si–O bond distances and O–Si–O bond angles, which range from 1.622(5) to 1.632(5) Å, and from 108.9(3) to 109.8(3)°, respectively, within the cage are in good agreement with previously reported values [3]. Within the MoO_6 octahedra, the Mo–O distances are grouped into three sets: Mo–O_t 1.667(5)–1.707(5) Å, average 1.689 Å; Mo–$O_{b,c}$ 1.810(5)–2.048(5) Å, average 1.932 Å; Mo–O_a 2.337(4)–2.372(4) Å, average 2.351 Å.

As can be seen from the bond distances and angles relevant to the Dy(III) coordination sphere, the Dy is seven-coordinate with a distorted pentagonal bipyramid of oxygen atoms, four from the NMP ligands, and the remaining three from coordinated water molecules. In the polyhedron of $[Dy(NMP)_4(H_2O)_3]^{3+}$ (Fig. 2), two oxygen atoms [O(2W), O(3W)] occupy the axial positions at distances of 2.2497(8) Å and 2.2264(9) Å and with the bond angle O(2W)–Dy(1)–O(3W) 167.5(5)°; the central Dy(1) is 0.0374 Å above the least-squares plane defined by O(1A), O(2A), O(3A), O(4A), and O(1W). The bond lengths of Dy–O are in the range 2.192(13)–2.368(8) Å, average 2.287 Å. The average Dy–$O_{(NMP)}$ bond distance, 2.282 Å, is a little shorter than the average Dy–$O_{(H_2O)}$ bond distance, 2.293 Å. The results indicate that the seven-coordinate Dy^{3+} ion is not compatible with the structure of the pentagonal bipyramid, owing to the interaction between the metal cation unit and the polyanion.

Comparing the structure of lanthanide-containing coordination cations of the title compound with other compounds [12,13], an important feature, lanthanide contraction, is confirmed by the following facts: first, the coordination number decreases from eight (La and Sm) to seven (Dy) with increasing atomic number; second, the average bond distances of Ln–O (Å) are 2.358 (La–O), 2.422 (Sm–O), 2.287 (Dy–O), respectively. The decrease of Ln–O average bond distances (Å) of these complexes in the series $La^{3+} > Sm^{3+} > Dy^{3+}$, is unexpected according to the increase in ionic radii

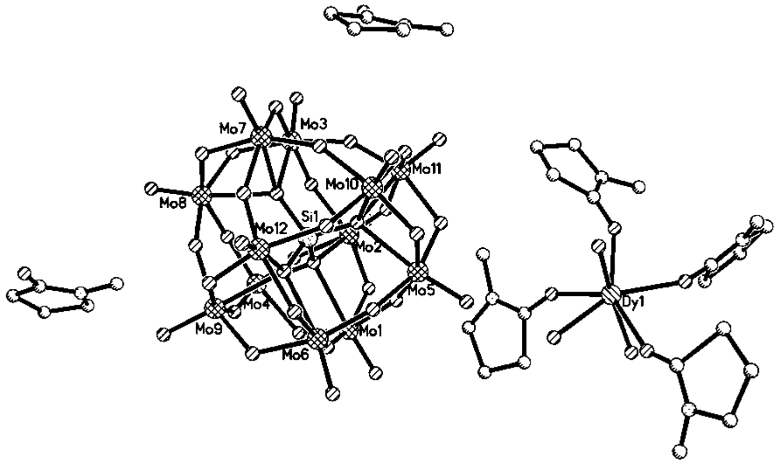

FIGURE 1 The structure of the title compound with partial labeling scheme. Hydrogen atoms are omitted for clarity.

TABLE I Selected bond lengths (Å) and bond angles (°) of the title compound

Si(1)–O(39)	1.622(5)	Si(1)–O(38)	1.628(5)
Si(1)–O(40)	1.630(5)	Si(1)–O(37)	1.632(5)
Mo(1)–O(1)	1.679(6)	Mo(1)–O(24)	1.815(5)
Mo(1)–O(17)	1.835(5)	Mo(1)–O(27)	2.014(5)
Mo(1)–O(28)	2.030(6)	Mo(1)–O(39)	2.352(5)
Mo(2)–O(2)	1.696(5)	Mo(2)–O(15)	1.815(5)
Mo(2)–O(29)	1.827(5)	Mo(2)–O(35)	2.011(5)
Mo(2)–O(23)	2.031(6)	Mo(2)–O(37)	2.325(5)
Mo(3)–O(3)	1.689(5)	Mo(3)–O(26)	1.821(5)
Mo(3)–O(35)	1.844(6)	Mo(3)–O(25)	2.001(6)
Mo(3)–O(21)	2.004(5)	Mo(3)–O(37)	2.350(5)
Mo(4)–O(4)	1.689(5)	Mo(4)–O(23)	1.816(5)
Mo(4)–O(30)	1.834(6)	Mo(4)–O(19)	2.023(5)
Mo(4)–O(22)	2.025(5)	Mo(4)–O(40)	2.331(5)
Mo(5)–O(5)	1.700(6)	Mo(5)–O(14)	1.817(5)
Mo(5)–O(27)	1.833(6)	Mo(5)–O(33)	1.993(6)
Mo(5)–O(13)	1.998(6)	Mo(5)–O(39)	2.329(5)
Mo(6)–O(6)	1.686(6)	Mo(6)–O(28)	1.825(5)
Mo(6)–O(16)	1.829(6)	Mo(6)–O(20)	2.003(6)
Mo(6)–O(31)	2.011(5)	Mo(6)–O(38)	2.326(5)
O(38)–Si(1)–O(40)	108.9(3)	O(39)–Si(1)–O(37)	109.7(3)
O(38)–Si(1)–O(37)	109.5(3)	O(40)–Si(1)–O(37)	109.8(3)
O(1)–Mo(1)–O(24)	103.3(3)	O(1)–Mo(1)–O(17)	102.5(3)
O(24)–Mo(1)–O(17)	98.2(2)	O(1)–Mo(1)–O(27)	99.5(3)
O(24)–Mo(1)–O(27)	85.3(2)	O(17)–Mo(1)–O(27)	156.3(2)
O(1)–Mo(1)–O(28)	97.9(3)	O(24)–Mo(1)–O(28)	156.4(2)
O(17)–Mo(1)–O(28)	87.0(2)	O(27)–Mo(1)–O(28)	81.1(2)
O(1)–Mo(1)–O(39)	169.7(2)	O(24)–Mo(1)–O(39)	87.0(2)
O(17)–Mo(1)–O(39)	75.29(19)	O(27)–Mo(1)–O(39)	81.50(19)
Dy(1)–O(4A)	2.254(6)	Dy(1)–O(2A)	2.267(7)
Dy(1)–O(3A)	2.279(8)	Dy(1)–O(2W)	2.320(7)
Dy(1)–O(1A)	2.33(2)	Dy(1)–O(1W)	2.368(8)
Dy(1)–O(3W)	2.192(13)	O(3W)–Dy(1)–O(2W)	167.5(5)
O(4A)–Dy(1)–O(3A)	76.0(3)	O(2A)–Dy(1)–O(3A)	73.2(3)
O(2A)–Dy(1)–O(1A)	78.8(6)	O(4A)–Dy(1)–O(1W)	73.5(3)
O(2W)–Dy(1)–O(1W)	93.7(3)	O(1A)–Dy(1)–O(1W)	70.7(6)

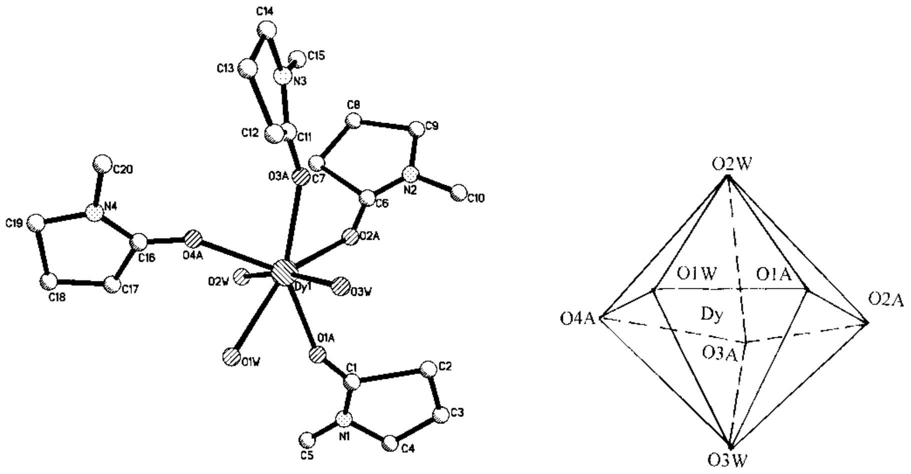

FIGURE 2 Coordination environment of Dy^{3+} in the $[Dy(NMP)_4(H_2O)_3]^{3+}$ cation with labeling scheme. Hydrogen atoms are omitted for clarity.

(Å): La^{3+} (1.17) > Sm^{3+} (1.10) > Dy^{3+} (1.05). A major cause of the lanthanide contraction is the electrostatic effect of increasing nuclear charge, imperfectly screened by the 4f electrons; however, owing to the empty electronic configuration $4f^0$ for La^{3+}, there is no screening effect, so La^{3+} binds firmly with ligands and the coordination ion is more stable. Finally, the considerable change in size of the Ln^{3+} ion means that homologous compounds of lanthanides with appreciably different radii may differ in structure. For $[Ln(NMP)_4(H_2O)_4]^{3+}$, coordinated ions with Ln = La and Sm have different structures: the La has a square antiprism geometry while the Sm has a distorted dodecahedral coordination.

There are four molecules of $[Dy(NMP)_4(H_2O)_3]H[SiMo_{12}O_{40}] \cdot 2NMP$ in a unit cell. Some hydrogen bonds are found in the packing diagram of the compound (Fig. 3): (a) hydrogen bonds of coordinated water molecules/terminal oxygen atoms of the polyanion (O···O distances 2.749–2.792 Å); (b) hydrogen bonds of coordinated water molecules/coordinated NMP molecules (O···O distances 2.786–2.821 Å). The presence of numerous heavy atoms in the structure precludes the determination of proton positions.

IR, UV and ESR Spectra

In the IR spectra, there are four asymmetric vibrations characteristic of heteropolyanions with a Keggin structure, namely, $\nu_{as}(Mo{=}O_t)$, $\nu_{as}(Mo{-}O_b)$, $\nu_{as}(Mo{-}O_c)$, and $\nu_{as}(Si{-}O_a)$, at 952, 860, 791, and 901 cm^{-1}, respectively. Comparing the IR spectra of the compound with those of $[Ln(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ (Ln = La, Sm) [12,13], the bands are similar. The results indicate that although the coordination cations are different in the two composites, their influences on the polyanion are identical. In addition, features at 1638, 1512, and 1115 cm^{-1} in the spectrum of the title compound are characteristic of *N*-methyl-2-pyrrolidone, and are assigned to $\nu_{as}(C{=}O)$, $\nu_{as}(C{-}N)$ and $\nu(N{-}CH_3)$ asymmetric stretching vibrations. Compared with the spectra of free NMP, $\nu_{as}(C{=}O)$ decreases 26 cm^{-1}, whereas $\nu_{as}(C{-}N)$ and $\nu(N{-}CH_3)$ increase slightly, indicating that NMP coordinates with Dy(III) ion through the oxygen atom of the C=O bond. This can be interpreted as the decreasing charge

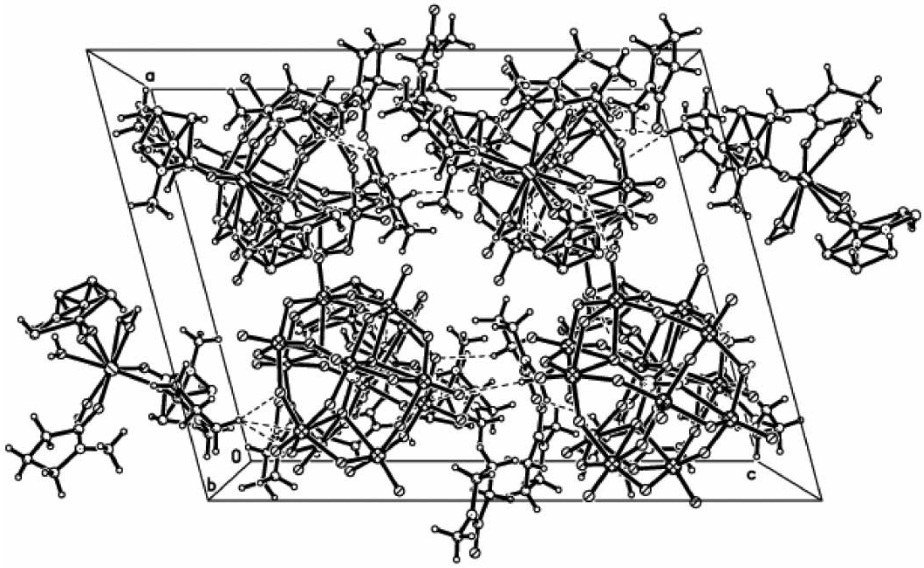

FIGURE 3 Packing diagram of the title compound viewed down the *b*-axis.

density over the oxygen of the C=O bonds leading to increased electron donation by methyl. The ν_{as}(C=O) value decreases 27, 30, and 26 cm^{-1} for compounds containing La, Sm, and Dy, respectively, which is consistent with the bond strength of Ln–O along the sequence Sm–O_{NMP} < La–O_{NMP} < Dy–O_{NMP}, and is compatible with the X-ray structure analysis for the average bond length of Ln–O_{NMP}: Sm–O_{NMP} (2.349 Å) > La–O_{NMP} (2.290 Å) > Dy–O_{NMP} (2.282 Å).

The spectra in the near UV of the title complex are to be found from 200 to 400 nm in the acetonitrile–water mixture (v/v = 2 : 1) solution. The absorption peak at 305 nm is weak and assigned to the $O_{b,c} \rightarrow$ Mo charge-transfer absorption band of the polyanion, and that at 240 nm is the $O_d \rightarrow$ Mo charge-transfer band. The results indicate that the interaction between heteropolyanion and coordinated ion is rather weak and the lanthanide-containing heteropolyanion complex practically decomposes in dilute solution. This was also observed in previous work [12].

Molybdenum is a favorable element for ESR spectroscopy. In the complex, the polyanion shows a shaped signal with the parameter $g = 1.9444$ (Fig. 4), which is typical of molybdenum(V) at 110 K [16,17] and assigned to the intervalence charge transfer ($Mo^{5+} \rightarrow Mo^{6+}$) band of $SiMo_{12}O_{40}^{4-}$. The result indicates that electron transfer occurs between the organic coordination cation and the polyanion and is carried by means of H-bonding, reducing $SiMo_{12}O_{40}^{4-}$ to blue heteropoly $SiMo_{12}O_{40}^{5-}$ with simultaneous oxidation of the organic coordinated cation. Comparing the ESR spectroscopy with that of the compounds (see [12,13]), the typical signal of molybdenum(V) with no hyperfine splitting from Mo is observed in the ESR signal, indicating electron delocalization.

Thermogravimetric Analysis

The TG analysis of the compound shows three steps (Fig. 5) for loss of weight: in the first step (from about 20 to 180°C), loss of 0.5 free NMP, weight loss 1.89%, and one

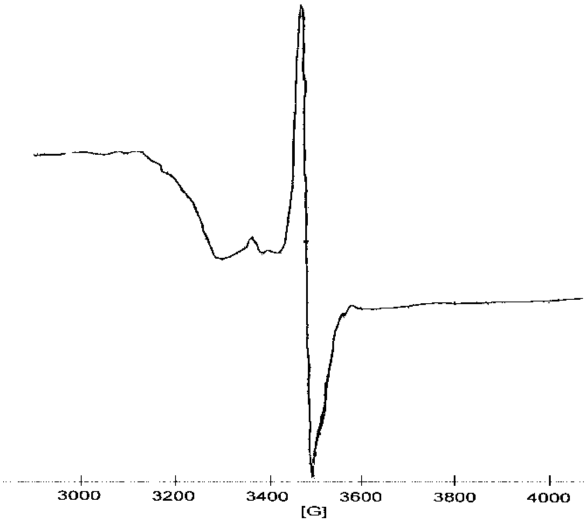

FIGURE 4 ESR spectra of the title compound at 110 K.

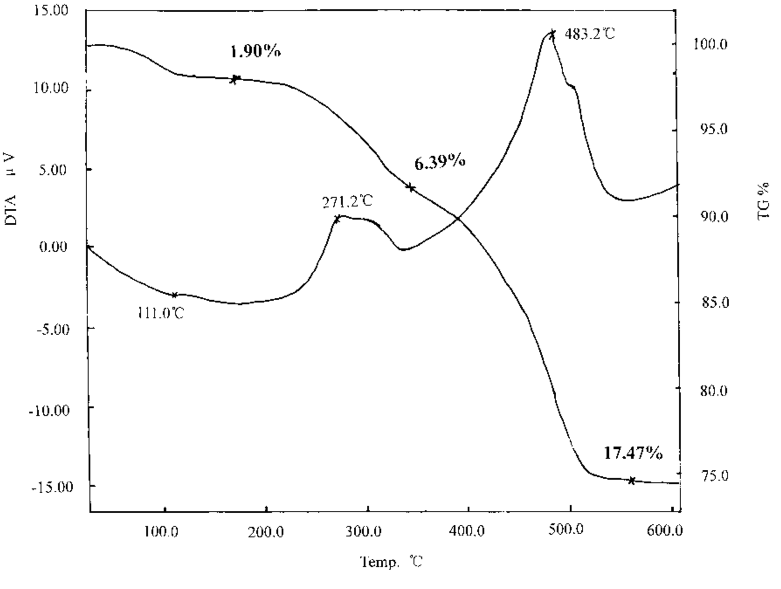

FIGURE 5 Thermogravimetric curves for the title compound.

exothermic peak at 111.0°C are observed in the DTA; in the second step (in the range 180–350°C), loss of the other 1.5 free NMP molecules and one coordination water, weight loss 6.39%, and one exothermic peak at 271.2°C corresponding to oxidation of NMP are observed; in the last step (350–580°C), loss of four coordinated NMPs and the other two coordinated water and half a structural water, weight loss 17.47% is observed. The result of thermogravimetric analysis is in good agreement with the structure determination. In the last step, one strong exothermic peak at 483.2°C is observed, due to breaking of the Dy–O bonds, with oxidation of organics and the beginning of decomposition of the heteropoly anionic cage to the lower oxides of the metals, such as MoO_3, and their slow volatilization [19].

CONCLUSION

In this paper we report the synthesis, characterization and crystal structure of a new complex formed by a coordinated lanthanide(III) unit and a heteropolymolybdate anion. Comparing this with previously published structures containing La and Sm [12,13], the coordinated ions are combined with the $[SiMo_{12}O_{40}]^{4-}$ anion by an electrostatic force. As a result of the lanthanide contraction, changes in coordination through the series from La to Dy are to be expected, and are confirmed by the coordination number and geometrical isomerism. The IR spectroscopies of compounds with La, Sm and Dy are compatible with the X-ray structure analysis.

Acknowledgments

This work was supported by the Natural Science Foundation of Henan Province and the outstanding Youth Foundation of Henan Province.

Supplementary Data

CCDC reference number 195686.

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