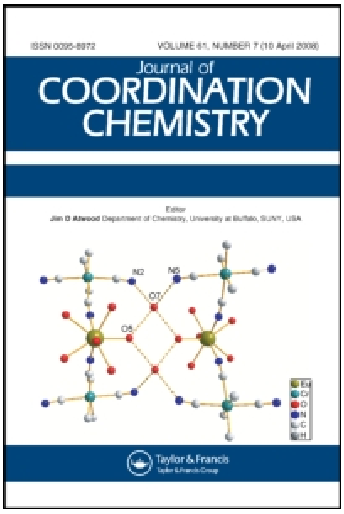

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A Novel Keggin Units-Supported Complex: Synthesis, Characterization and Crystal Structure of $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2] \cdot 2DMF$

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A NOVEL KEGGIN UNITS-SUPPORTED COMPLEX: SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2] \cdot 2DMF$

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A novel hybrid compound, $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2] \cdot 2DMF$, has been synthesized from $H_4GeW_{12}O_{40} \cdot nH_2O$, $CuCl_2$ and *N,N*-dimethylformamide (DMF) in aqueous solution and characterized by elemental analysis, UV and IR spectra. Single crystal X-ray structure analysis shows that the crystal consists of a α-Keggin heteropolyanion-supported anion $[Cu(DMF)_4(GeW_{12}O_{40}^{4-})_2]^{6-}$, two free *N,N*-dimethylformamide molecules, six protonated dimethylamine (DMA) molecules, and that the coordinating atoms of DMF are the oxygen atoms of C=O group. Thermal analysis indicates that the thermal stability of the $GeW_{12}O_{40}^{4-}$ anion in the title compound is stronger than that in acid.

Keywords: Keggin structure; Crystal structure; Hybrid compound; Heteropolyanion-supported

INTRODUCTION

Polyoxometalates are widely studied owing to their interesting applications in catalysis, electrical conductivity, magnetism, nonlinear optical properties and medicine [1–6]. Recent investigations of molecular design led to important advances in the field of transition-metal substituted polyoxometalates and polyoxometalate-supported inorganic and organometallic complexes [7–11]. A number of novel complexes based on polyoxometalate anions have been reported and their crystal structures characterized, for examples: $[Cu(phen)_2]_2[\{Cu(phen)\}_2Mo_8O_{26}] \cdot H_2O$ [9], which has a discrete cluster structure; $[\{Cu(4,4'\text{-bipy})\}_4Mo_8O_{26}]$ [10] and $[\{Cu(en)\}_2Mo_8O_{26}]$ [11], which possess infinite extended structures. To our knowledge, no previous structural examples of transition metal complexes coordinated to a Keggin anion prepared by normal synthesis have been reported. Two complexes $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$ and $[Co(1,10'\text{-phen})_3]_{1.5}[PMo_{12}O_{40}Co(1,10'\text{-phen})_2(H_2O)] \cdot 0.5H_2O$ were prepared by hydrothermal synthesis [12].

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Here, we report the synthesis, spectroscopic characterization, thermal behavior and X-ray crystal structure of a α-Keggin heteropolyanion-supported copper-*N*,*N*-dimethylformamide complex, $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2]\cdot 2DMF$. The structure determination of $[Cu(DMF)_4(GeW_{12}O_{40})_2]^{6-}$ indicates a novel α-Keggin heteropolyanion coordinated to a transition metal complex.

EXPERIMENTAL

Materials

All organic solvents used for synthesis and physical measurements were reagent grade and used without purification. The $H_4GeW_{12}O_{40}\cdot nH_2O$ was prepared by literature method and confirmed by IR and UV spectra [13].

Physical Measurements and Analyses

C, H and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra of samples were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrometer in the range 4000–500 cm^{-1}. The UV spectra were observed in aqueous solution with a UV-250 spectrometer. Thermogravimetric analysis (TG-DTA) was performed in air on a Perkin Elmer-7 instrument with a heating rate of 10°C/min. All measurements were made at room temperature.

Preparation of the Title Compound

2.0 g of $H_4GeW_{12}O_{40}\cdot nH_2O$ was dissolved in 10 mL of water, and 0.2 g $CuCl_2\cdot 2H_2O$ was added at 90°C with stirring until the solution was nearly dry, and then, the solid was isolated, and dried on fritted-glass funnel. 2.0 g of this dried powder of copper salts were dissolved in 10 mL of acetonitrile and water in the ratio of 5 : 2 (v/v), and 1 mL DMF liquid was added at 70°C; the stirring mixture was reacted for 15 min. After cooling to room temperature, the solution was filtered off and evaporated at room temperature. Three days later, green block crystals were isolated. The yield of the title compound is 75% based on $H_4GeW_{12}O_{40}\cdot nH_2O$. Anal. Calcd. For $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2]\cdot 2DMF$ (%): C, 6.40; H, 1.40; N, 2.50. Found: C, 6.00; H, 1.10; N, 2.39%.

X-ray Structure Determination of the Title Compound

The crystal data for $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2]\cdot 2DMF$ (monoclinic, space group $P2_1/c$) are: $M = 6616.2090\,\text{g mol}^{-1}$, $a = 13.586(3)$ Å, $b = 20.015(4)$ Å, $c = 20.524(4)$ Å, $\beta = 104.88(3)°$, $V = 5394.1(19)$ Å^3, $Dc = 4.070\,\text{g/cm}^3$, $Z = 2$, $F(000) = 5810$. A single crystal of dimensions $0.25 \times 0.22 \times 0.20$ mm was used for the data collection on a Rigaku RAXIS-IV image plate area detector with Mo-Kα ($\lambda = 0.71073$ Å). A total of 17877 reflections were collected ($1.45 < \theta < 27.57°$, $0 \leq h \leq 17$, $-25 \leq k \leq 26$, $-26 \leq l \leq 24$); 10715 reflections were unique. The structure was solved by direct methods and refined using full-matrix least-squares calculations with anistropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. The refinement converged at $R = 0.0666$ over 10764 reflections with $I \geq 2\sigma(I)$, $wR = 0.1449$, $w^{-1} = [\sigma^2(F_0{}^2) + (0.082P)^2]$ (where $P = (F_o^2 + {}^2F_c^2)/3$). The largest remaining difference peak and hole were 3.003 and $-3.655\,\text{e}\text{Å}^{-3}$, respectively. All calculations were performed using the SHELXTL-97 program [14].

RESULTS AND DISCUSSION

Synthesis

The good quality and stable crystals of the title compound are obtained from a mixed solvent of acetonitrile and water at room temperature. The selection of suitable solvent was the key point for crystal growth of the title compound. By controlling the ratio of acetonitrile and water to make the crystals grow slowly, ideal crystals were obtained. The crystals are sensitive to sunlight, probably because the polyanion is a good electron-acceptor, while *N*,*N*-dimethylformamide is a rich electron-donor, such that electron transfer can occur in the presence of sunlight, leading to mixed-valence compound. Therefore, exposure of the solution to sunlight should be avoided.

IR and UV Spectra

The IR spectra show absorptions of the title compound at 1644(vs), 1496(w), 966(vs), 886(vs), 830(m) and 777(vs), which can be assigned to the ν(C=O), ν(C–N), δ(C–N), ν(W–O_d), ν(W–O_b), ν(Ge–O_a) and ν(W–O_c) vibrations, respectively. Comparing the IR spectra of the title compound with that of α-$H_4GeW_{12}O_{40} \cdot nH_2O$ [13], the vibration band of the W=O_d bond in the title compound has a red-shift from 980 to 966 cm^{-1}; the Ge–O_a bond has a blue-shift from 818 to 830 cm^{-1}; the W–O_b bond has a blue-shift from 883 to 886 cm^{-1}; and the W–O_c bond has a blue-shift from 760 to 777 cm^{-1}. The spectra indicate that the polyanions of the title compound still maintain a basic Keggin structure, but their structures are distorted due to coordination. In addition, comparing the IR spectra of the title compound with that of free DMF [15], the vibration band of C=O in the title compound red shifts from 1678 to 1644 cm^{-1}. The result verifies that the coordinating atoms of DMF are oxygen atoms of the C=O group and their nitrogen atoms are not involved in coordination. They are also in agreement with the results of the single crystal X-ray diffraction analysis.

The UV spectra of the title compound in aqueous solution and in acetonitrile and water (v/v = 5 : 2) exhibit absorption peaks at 190, 265 and 225 nm/265 nm. The absorption at 265 nm, indicates that the interactions between heteropolyanion and coordinated ion are rather weak and the complex is almost disrupted in solution. The charge transfer absorption of $O_d \rightarrow W$ has a red shift from 190 to 225 nm, while $O_{b,c} \rightarrow W$ are almost alike. The latter is the characteristic spectrum of the heteropolyacid, which is not affected by anion protonation; but the former is affected by the different electrolyte in solution [16].

X-ray Structure of the Title Compound

The structure of the title compound is given in Fig. 1. The coordination environment of copper(II) is given in Fig. 2. The packing diagram of the title compound is given in Fig. 3. Selected bond lengths and angles are listed in Tables I and II, respectively.

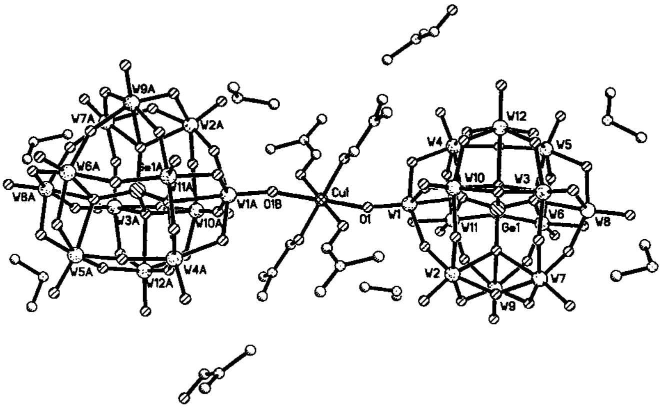

FIGURE 1 The structure of the title compound with partial labeling scheme. Hydrogen atoms are omitted for clarity.

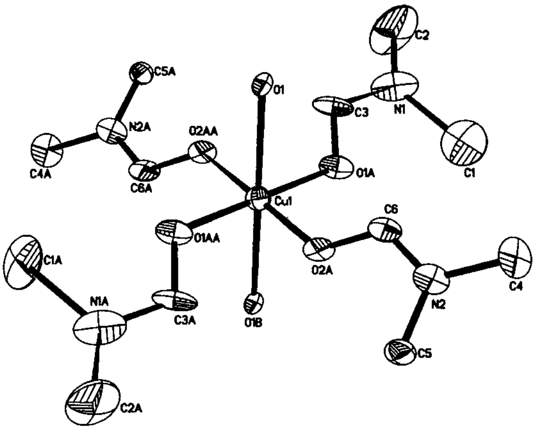

FIGURE 2 Coordination environment of Cu^{2+} in the title compound with labeling scheme. Hydrogen atoms are omitted for clarity.

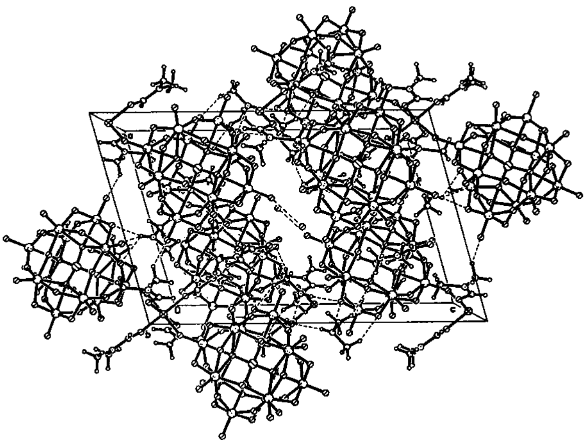

FIGURE 3 Packing diagram of $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2]\cdot 2DMF$ viewed down along the *b*-axis.

TABLE I Selected bondlengths (Å) of the title compound

W(1)–O(1)	1.689(14)	W(2)–O(2)	1.690(14)
W(1)–O(15)	1.895(15)	W(2)–O(17)	1.974(14)
W(1)–O(30)	1.910(14)	W(2)–O(19)	1.962(15)
W(1)–O(23)	1.945(15)	W(2)–O(23)	1.903(14)
W(1)–O(32)	1.969(15)	W(2)–O(35)	1.883(13)
W(1)–O(39)	2.290(13)	W(2)–O(37)	2.286(13)
W(3)–O(3)	1.692(16)	W(4)–O(4)	1.721(17)
W(3)–O(24)	1.899(15)	W(4)–O(36)	1.916(15)
W(3)–O(34)	1.949(14)	W(4)–O(15)	1.955(14)
W(3)–O(33)	1.894(15)	W(4)–O(13)	1.905(15)
W(3)–O(18)	1.921(15)	W(4)–O(26)	1.926(14)
W(3)–O(40)	2.291(12)	W(4)–O(39)	2.291(13)
W(5)–O(5)	1.675(17)	W(6)–O(6)	1.709(17)
W(5)–O(36)	1.918(14)	W(6)–O(25)	1.933(14)
W(5)–O(22)	1.966(16)	W(6)–O(16)	1.960(14)
W(5)–O(16)	1.893(15)	W(6)–O(29)	1.886(14)
W(5)–O(28)	1.965(16)	W(6)–O(31)	1.937(15)
W(5)–O(38)	2.312(12)	W(6)–O(38)	2.292(13)
Cu(1)–O(2A)	1.938(15)	Ge(1)–O(40)	1.730(13)
Cu(1)–O(1A)	1.970(17)	Ge(1)–O(37)	1.734(13)
Cu(1)–O(1)	2.443(16)	Ge(1)–O(38)	1.743(12)
N(4)–C(11)	1.43(4)	Ge(1)–O(39)	1.751(13)
N(4)–C(10)	1.44(3)	N(6)–C(15)	1.45(4)
N(5)–C(13)	1.47(3)	N(6)–C(14)	1.55(6)
N(5)–C(12)	1.50(4)		

TABLE II Selected bond angle (°) of the title compound

O(1)–W(1)–O(15)	100.8(7)	O(32)–W(1)–O(39)	72.0(5)
O(1)–W(1)–O(30)	103.3(6)	O(40)–Ge(1)–O(37)	109.7(6)
O(15)–W(1)–O(30)	90.7(6)	O(40)–Ge(1)–O(38)	109.1(6)
O(1)–W(1)–O(23)	101.7(6)	O(37)–Ge(1)–O(38)	108.7(6)
O(15)–W(1)–O(23)	157.4(6)	O(38)–Ge(1)–O(39)	109.9(6)
O(30)–W(1)–O(23)	84.4(6)	O(2A)#1–Cu(1)–O(2A)	180.0(2)
O(1)–W(1)–O(32)	99.9(7)	O(2A)#1–Cu(1)–O(1A)	89.7(6)
O(15)–W(1)–O(32)	88.8(6)	O(2A)–Cu(1)–O(1A)	90.3(6)
O(30)–W(1)–O(32)	156.5(6)	O(2A)#1–Cu(1)–O(1A)#1	90.3(6)
O(23)–W(1)–O(32)	87.1(6)	O(2A)–Cu(1)–O(1A)#1	89.7(6)
O(1)–W(1)–O(39)	169.8(6)	O(1A)–Cu(1)–O(1A)#1	180.0(8)
O(15)–W(1)–O(39)	73.3(5)	C(11)–N(4)–C(10)	114(2)
O(30)–W(1)–O(39)	85.3(5)	C(13)–N(5)–C(12)	111(2)
O(23)–W(1)–O(39)	84.4(5)	C(15)–N(6)–C(14)	107(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z$.

The structure of the $[\{Cu(DMF)_4\}(GeW_{12}O_{40})_2]^{6-}$ anion consists of two anionic Keggin $GeW_{12}O_{40}^{4-}$ units which are each coordinated through a bridging O atom, O(1), to the central Cu atom of the Cu $(DMF)_4^{2+}$ cation. The molecular geometry of this polyanion is constrained by the fact that the Cu ion lies on a crystallographic center of inversion. The remainder of the crystal lattice contains discrete DMF molecules and protonated DMA cations, which are known for a Keggin structure [17] which is formed from a central GeO_4 tetrahedron whose O atoms are part of the cage of surrounding twelve WO_6 octahedra linked to each other by sharing corners and edges.

The W(1)–O(1) and Cu(1)–O(1) bond distances for the bridging O atom are 1.689(14) Å and 2.443(16) Å, respectively. The Ge–O bond distances and O–Ge–O bond angles, which range from 1.730(13)–1.751(13) Å and from 108.7(6)–109.9(6)°, respectively, within the cage are in good agreement with previously reported values [18]. Within the WO_6 octahedra, the W–O distances are grouped into three sets: W–O_t 1.6758(17)–1.721(17) Å, W–O_b 1.883(13)–1.974(14) Å, W–O_a 2.281(12)–2.314(13) Å, whereas the O–W–O bond angles range from 72.0(5)–172.2(7)°. The two unique Cu–O (DMF) distances within the $Cu(DMF)_4^{2+}$ cation are 1.983(15) and 1.970(17) Å with the two independent O(DMF)–Cu–O(DMF) bond angles of 90.3(6)° and 89.7(6)° consistent with a square planar disposition of the four DMF molecules about the copper. The Cu(1)–O(1) bond being approximately 0.5 Å longer than the two independent Cu–O(DMF) bonds indicates that the molecular structure of the central CuO_6 octahedron is tetragonally distorted due to the Jahn-Teller effect and explains the ease with which this hexaanion undergoes dissociation in solution.

There are four molecules of $[(CH_3)_2NH_2]_6[\{Cu(DMF)_4\}(GeW_{12}O_{40})_2] \cdot 2DMF$ in a unit cell. Unexpectedly there are no hydrogen bonds in the molecule. The dashed lines in the packing diagram in Fig. 4 show the shortest contacts. The shortest contact involves the N atoms of DMA and the O atoms of polyanion. The involved oxygen atoms of the anion are the terminal oxygen atoms and the one type of bridging oxygen atoms. They are O8–N6 (2.850 Å), O34–N5 (2.947 Å) and O23-N4 (2.942 Å), respectively.

The presence of a numerous heavy atoms in the structure precludes the determination of the hydrogen atom positions. Although we cannot determine the sites of the H^+ of $H_4GeW_{12}O_{40} \cdot nH_2O$ from the X-ray structure, based on the bond valence parameters [19], the bond orders for the N atoms in the molecule are determined by fitting Eq. (1)

$$V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r'_0 - r_{ij}}{B}\right) \tag{1}$$

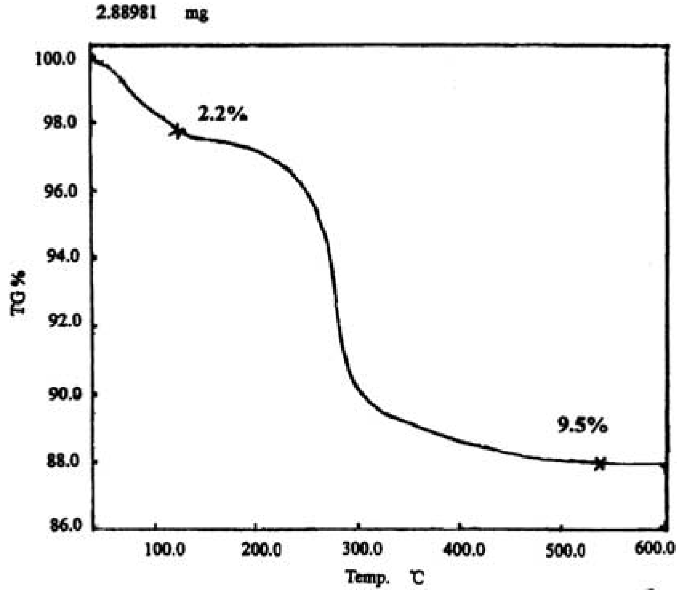

FIGURE 4 Thermo-gravimetric curve for the title compound.

(relating V_i, the oxidation state of cation i, to S_{ij}, the valence of the bond between the cation i and the anion j). By refining B it is found that B could rarely be determined to better than 0.05 and that a value of 0.37 was consistent with most or all of the refined values. By assuming this value for B, only one parameter (r_0) remains to be fitted and this can be done exactly for each cation environment by solving Eq. (1) for r'_0. A value of r'_0 is calculated for each cation environment in the ICSD in which the ligands are chemically identical and in which there is no disorder. The resultant values are then averaged to give the best value for r_0 for a given ion pair. The bond orders for N atoms of DMA molecule are 3.33 (N1), 2.97 (N2), 3.12 (N3), 2.03 (N4), 1.78 (N5) and 1.72 (N6), respectively. That suggests that every DMA has combined with a H^+ on N4, N5 and N6 and their symmetry-related partner, respectively. So we presume that the N atom in each DMA is protonated to form the $[(CH_3)_2NH_2]^+$ cation.

Thermo-Gravimetric Analysis

The thermal behavior of the title compound was studied in the range of 30–600°C (see Fig. 4). The result of the thermo-gravimetric analysis is basically in agreement with the structure determination. The TG analysis of the title compound shows two steps for loss of weight, which suggests a multiple-stage decomposition process: heating from about 30 to 120°C leads to the loss of two free DMF molecules (weight loss *ca.* 2.2%), and an exothermal peak at 110.5°C is observed in the DTA; from about 120 to 540°C the loss of four coordinated DMF and six protonated DMA and three consitution water molecules (weigh loss *ca.* 9.3%) are observed. In the second step, one exothermal peak at 279.7°C and one strong exothermal peak at 526.2°C are observed. The exothermal peak at 279.7°C corresponds to oxidation of four coordinated DMF molecules and the exothermal peak at 526.2°C represents the decomposition of heteropolyanion $GeW_{12}O_{40}^{4-}$. The data indicate the stability of the $GeW_{12}O_{40}^{4-}$ anion is stronger in the title compound than that in the acid.

Acknowledgments

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