

Hydrothermal synthesis, structure and quantum chemistry of transition metal complex supported by metal-oxo cluster $[\{\text{Ni}(\text{phen})_2\}_2(\xi\text{-Mo}_8\text{O}_{26})]$

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Abstract A nickel-1,10-phenanthroline complex supported on an octamolybdate, $[\{\text{Ni}(\text{phen})_2\}_2(\xi\text{-Mo}_8\text{O}_{26})]$, has been hydrothermally synthesized with MoO_3 , H_2MoO_4 , $\text{Ni}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ and 1,10-phenanthroline (1,10-phen) as raw materials. The crystals of the compound belong to monoclinic $\text{P}2_1/n$ space group, $a = 1.2952(2)$, $b = 1.6659(10)$, $c = 1.3956(12)$ nm, $\beta = 106.273(8)^\circ$, $V = 2.8906(5)$ nm³, $Z = 2$. 5604 observable reflections ($I > 2\sigma(I)$) were used for structure resolution and refinements to converge to final $R_1 = 0.0414$, $wR_2 = 0.0815$. The result of structure determination shows that the compound contains octamolybdate possessing a novel structure type (named as ξ -isomer). The feature of $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ is that it is composed of Mo_6O_6 ring and two MoO_6 octahedra located at cap positions on opposite faces. The Mo_6O_6 ring contains two octahedral and four trigonal-bipyramidal Mo^{VI} atoms. Each $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ unit is bonded with two $[\text{Ni}(\text{phen})_2]^{2+}$ through terminal oxygen atoms of octahedral and neighbouring trigonal-bipyramidal Mo atom in the Mo_6O_6 ring. IR and UV-Vis spectra of the compound were measured and its electronic structure was studied by EHMO method.

Keywords: metal-oxo cluster, supporting, transition metal complex, ξ -octamolybdate.

Metal-oxo cluster chemistry has aroused interest for a long time owing to development of the chemistry itself and its many kinds of applications in fields such as catalysis, electric conductivity, magnetism, nonlinear optical properties and medicine^[1,2]. Recently, an important progress in metal oxide cluster chemistry has just been made on polyoxoanion-supported inorganic and organometallic complexes. The syntheses and structures of some such complexes have been reported, for example, inorganic coordination compounds $[\{\text{Cu}(4,4'\text{-bipy})\}_4(\text{Mo}_8\text{O}_{26})]^{3-}$ and $[\text{Cu}(\text{en})(\text{V}_2\text{O}_6)]^{4-}$, which possess infinite extended structures; $[\text{Zn}(2,2'\text{-bipy})_2(\text{V}_4\text{O}_{12})]^{5-}$ and $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ ^[6], which are molecular clusters, and organometallic compounds $[(\text{CO})_3\text{Mn}(\text{cis-Nb}_2\text{W}_4\text{O}_{19})]^{3-}$ ^[7] and $[\{(\eta\text{-C}_5\text{Me}_5)\text{Rh}\}(\text{Mo}_{13}\text{O}_{40})]^{2+}$ ^[8], etc.

We report here the synthesis and characterization of a novel nickel-phenanthroline complex supported on octamolybdate, $[\{\text{Ni}(\text{phen})_2\}_2(\xi\text{-Mo}_8\text{O}_{26})]$ (**1**). To date, many reports on syntheses

and structures of the compounds containing α -, β - and γ -[Mo₈O₂₆]⁴⁻ isomer have been presented. Recently, Isobe^[9] reported the first compound having δ -[Mo₈O₂₆]⁴⁻ isomer, [(η -C₅Me₅Rh)₂-(μ ₂-SCH₃)₃]₄[Mo₈O₂₆]⁴⁻ • 2CH₃CN, and then Zubietta^[3] reported syntheses and structures of the other compounds having δ -[Mo₈O₂₆]⁴⁻ isomer [{Cu(4,4'-bipy)]₄(Mo₈O₂₆)] and the first compound containing ε -[Mo₈O₂₆]⁴⁻ isomer [{Ni(H₂O)₂(4,4'-bipy)₂]₂(Mo₈O₂₆)]. The result of structure determination for compound **1** indicates that it contains a novel unprecedented octamolybdate isomer named ξ -[Mo₈O₂₆]⁴⁻.

1 Experimental and structure analysis

1.1 Synthesis of the compound

The title compound was synthesized using the hydrothermal method. A mixture of MoO₃, H₂MoO₄, Ni(OAc)₂•6H₂O, phen and H₂O in the molar ratio 1.0 : 1.0 : 0.8 : 1.6 : 450 was fully stirred at room temperature, and sealed in a Teflon lined stainless steel reactor and heated at 170 °C for three days. The purple block crystals were obtained after the reaction system slowly cooled to room temperature and filtered. The yield is ca. 35% (based on Mo). Elemental analyses calculated for C₄₈H₃₂N₈O₂₆Ni₂Mo₈(%): C, 28.49; H, 1.58; N, 5.53; Ni, 5.83; Mo, 37.96; found (%): C, 28.44; H, 1.52; N, 5.47; Ni, 5.76; Mo, 37.12.

1.2 Structure analysis

A purple single crystal with the dimension of 0.22 mm × 0.24 mm × 0.40 mm was mounted on a Bruker P4 four-circle diffractometer for reflection data collection under ω - 2θ scan mode MoK α radiation ($\lambda = 0.07017$ nm) monochromatized by a graphite monochromator. The total number of reflections measured in the range of $1.96^\circ \leq \theta \leq 26.00^\circ$ was 7944, of which 5604 were considered as the observed ($I > 2\sigma(I)$) and used for structure resolution and refinements. The correction of Lp factor and absorption effect was applied to all reflection data. Crystallographic data: monoclinic system, $a = 1.2952(2)$, $b = 1.6659(1)$, $c = 1.3956(1)$ nm, $\beta = 106.273(8)^\circ$, $V = 2.8906(5)$ nm³, space group P2₁/n, $Z = 2$, $D_c = 2.323$ g • cm⁻³ and $F(000) = 1952$. The crystal structure was solved by direct methods and refined with full-matrix least squares program to converge finally to $R_1 = 0.0414$, $wR_2 = 0.0815$, $S = 1.058$, $\Delta\rho_{\max} = 0.630$ (e • nm • 10³) and $\Delta\rho_{\min} = -0.866$ (e • nm • 10³). All computations were performed by using SHELXTL (Version 5) program system on a PC-486 computer.

1.3 Characterizations of the compound

(i) IR spectra. The IR spectra were recorded on KBr with a Perkin Elemer 783 infrared spectrophotometer. There are obvious characteristic absorptions at 945($\nu_{\text{Mo-O}(t)}$), 885($\nu_{\text{Mo-O}(Ni)}$), 850($\nu_{\text{Mo-O}(\mu_2)}$) and 705 cm⁻¹($\nu_{\text{Mo-O}(\mu_3)}$).

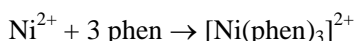
(ii) UV-Vis spectra. The UV-Vis spectra of the title compound were observed in DMF solu-

tion with a concentration of 1.0×10^{-3} mol/L on a UV-3100 UV-Vis-NIR spectrophotometer. λ_{\max} ($\epsilon/L \cdot \text{mol} \cdot \text{cm}^{-1}$): 340 (6.0×10^2), 585 nm (2.15×10^2). The former is assigned to O \rightarrow M charge transfer peak and the latter belongs to d \rightarrow d transition band.

2 Results and discussion

2.1 Synthesis

It was found that synthetic result was remarkably affected by the raw material ratio. Compound **1** was synthesized in the mole ratio of Ni(OAc)₂ : phen = 1 : 2. When Ni(OAc)₂ : phen \leq 1 : 3, however, non-supported ion cluster compound, [Ni(phen)₃]₂[Mo₈O₂₆], was easily produced. In this case the following reaction occurred:



Owing to coordination-saturated complex cation [Ni(phen)₃]²⁺ forming, coordination between nickel cation and terminal oxygen of cluster anion [Mo₈O₂₆]⁴⁻ cannot take place and the complex supported by metal-oxo cluster will not be produced.

The pH value of the reaction solution is important for obtaining crystal product. Compound **1** was produced in pH=7.0. When pH is over large or small, a precipitate forms easily, and it is difficult to obtain crystal product of compound **1**.

2.2 Structure

The non-hydrogen atomic coordinates and equivalent isotropic displacement parameters, selected bond lengths and bond angles, are listed in tables 1–3, respectively. The molecular structure of compound **1** is given in fig. 1.

The crystal of the compound consists of discrete heterometallic decanuclear clusters $[\{\text{Ni}(\text{phen})_2\}_2(\text{Mo}_8\text{O}_{26})]$ (fig. 1). The octamolybdate anion in **1** possesses a novel unprecedented structure mode named ξ -[Mo₈O₂₆]⁴⁻ isomer, which is composed of a MoO₆ ring Mo1, Mo4, Mo2, Mo1A, Mo4A and Mo2A capped on opposite faces by two MoO₆ octahedra (Mo3 and Mo3A). The structure characteristic feature of ξ -octamolybdate isomer is that the Mo₆O₆ ring contains two octahedral and four trigonal-bipyramidal Mo^{VI} atoms. In the ring, linkage between any two MoO₅ trigonal bipyramids is edge-shared, while that between any MoO₆ octahedron and MoO₅ trigonal bipyramid is corner-shared. Each capping MoO₆ octahedron is linked to two MoO₆ octahedra and a MoO₅ trigonal bipyramid in the Mo₆O₆ ring by edge-sharing and to another MoO₅ trigonal bipyramid of the ring by corner-sharing. Two capping MoO₆ octahedra are linked to each other by edge-sharing. The structure features of ξ -[Mo₈O₂₆]⁴⁻ in compound **1** are obviously different from those of other octamolybdate isomers synthesized. For example, the α -[Mo₈O₂₆]⁴⁻ consists of six MoO₆ octahedra and two MoO₄ tetrahedra; the β -[Mo₈O₂₆]⁴⁻ is composed of eight MoO₆ octahedra by edge-sharing; the γ -[Mo₈O₂₆]⁴⁻ contains six MoO₆ octahedra and two MoO₅ trigonal bipyramids; the δ -[Mo₈O₂₆]⁴⁻ has four MoO₆ octahedra and four MoO₄ tetrahedra^[3, 9], and the

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement ($\times 10^5 \text{ nm}^2$)^{a)}

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|-----|-----------|------------|------------|---------------|
| Mo1 | 697 (1) | 925 (1) | 1845 (1) | 23 (1) |
| Mo2 | 1787 (1) | 285 (1) | -1547 (1) | 24 (1) |
| Mo3 | -263 (1) | 854 (1) | -732 (1) | 22 (1) |
| Mo4 | 2528 (1) | 1078 (1) | 664 (1) | 27 (1) |
| Ni1 | 1621 (2) | -1783 (1) | -2510 (1) | 27 (1) |
| O1 | 1155 (7) | 1186 (5) | -658 (7) | 23 (2) |
| O2 | 2825 (8) | 314 (6) | -349 (7) | 37 (2) |
| O3 | -1065 (8) | 1365 (5) | -1709 (7) | 33 (2) |
| O4 | -334 (7) | -18 (5) | 1673 (7) | 26 (2) |
| O5 | 1931 (8) | 999 (6) | -2357 (7) | 33 (2) |
| O6 | 1615 (8) | 1590 (5) | 1372 (7) | 30 (2) |
| O7 | 1599 (9) | 534 (6) | 2879 (7) | 38 (2) |
| O8 | 2065 (8) | -617 (6) | -2039 (7) | 34 (2) |
| O9 | 3298 (9) | 559 (7) | 1642 (8) | 44 (3) |
| O10 | 1008 (7) | 146 (5) | 733 (7) | 27 (2) |
| O11 | -491 (7) | 1299 (5) | 314 (7) | 28 (2) |
| O12 | -123 (8) | 1552 (5) | 2312 (7) | 30 (2) |
| O13 | 3288 (9) | 1867 (6) | 515 (8) | 40 (3) |
| N1 | 3021 (8) | -1900 (6) | -2915 (8) | 24 (2) |
| N2 | 1071 (10) | -1418 (7) | -3980 (9) | 32 (3) |
| C1 | 3999 (12) | -2123 (9) | -2368 (11) | 36 (3) |
| C2 | 4879 (12) | -2172 (9) | -2744 (12) | 38 (3) |
| C3 | 4733 (12) | -1994 (8) | -3729 (12) | 37 (3) |
| C4 | 3745 (12) | -1756 (8) | -4333 (12) | 34 (3) |
| C5 | 3520 (13) | -1531 (9) | -5368 (12) | 38 (3) |
| C6 | 2531 (14) | -1291 (10) | -5907 (11) | 43 (4) |
| C7 | 1675 (14) | -1237 (8) | -5464 (10) | 36 (3) |
| C8 | 1884 (11) | -1444 (8) | -4443 (10) | 28 (3) |
| C9 | 2898 (11) | -1701 (7) | -3897 (10) | 28 (3) |
| C10 | 608 (15) | -1006 (10) | -6001 (11) | 46 (4) |
| C11 | -150 (11) | -983 (10) | -5502 (10) | 39 (4) |
| C12 | 85 (15) | -1206 (10) | -4493 (11) | 43 (4) |
| N3 | 1104 (10) | -2976 (7) | -2764 (10) | 35 (3) |
| N4 | 2157 (10) | -2206 (7) | -1065 (9) | 34 (3) |
| C13 | 650 (12) | -3357 (9) | -3591 (12) | 40 (4) |
| C14 | 293 (13) | -4156 (11) | -3576 (14) | 50 (5) |
| C15 | 400 (16) | -4530 (11) | -2731 (14) | 68 (6) |
| C16 | 911 (14) | -4155 (9) | -1821 (15) | 49 (4) |
| C17 | 1300 (12) | -3371 (8) | -1845 (13) | 38 (4) |
| C18 | 1099 (16) | -4522 (10) | -832 (15) | 58 (5) |
| C19 | 1578 (12) | -4125 (12) | -14 (10) | 80 (8) |
| C20 | 1949 (12) | -3334 (10) | -47 (12) | 39 (4) |
| C21 | 1823 (12) | -2950 (8) | -969 (11) | 33 (3) |
| C22 | 2480 (12) | -2889 (11) | 812 (12) | 46 (4) |
| C23 | 2846 (14) | -2128 (12) | 724 (12) | 49 (4) |
| C24 | 2707 (12) | -1816 (10) | -218 (11) | 38 (3) |

a) $U(\text{eq})=(U_{11}+U_{22}+U_{33})/3$.

Table 2 Selected bond lengths / nm

| | | | |
|----------------------|-------------|-----------------------|-------------|
| Mo1-O7 | 0.1711(11) | Mo1-O12 | 0.1740 (9) |
| Mo1-O6 | 0.1876 (9) | Mo1-O4 | 0.2032 (8) |
| Mo1-O10 | 0.2146 (8) | Mo1-O11 | 0.2341 (10) |
| Mo2-O5 | 0.1687 (9) | Mo2-O8 | 0.1731 (9) |
| Mo2-O2 | 0.1830 (10) | Mo2-O4 ^{a)} | 0.1894 (9) |
| Mo2-O1 | 0.2244 (8) | Mo3-O3 | 0.1694 (10) |
| Mo3-O1 | 0.1892 (8) | Mo3-O11 | 0.1734 (8) |
| Mo3-O4 ^{a)} | 0.2197 (8) | Mo3-O10 ^{a)} | 0.1926 (8) |
| Mo3-O10 | 0.2529 (8) | Mo4-O9 | 0.1685 (10) |
| Mo4-O13 | 0.1690 (9) | Mo4-O6 | 0.1939 (9) |
| Mo4-O2 | 0.2018 (10) | Mo4-O1 | 0.2182 (9) |
| Ni1-N1 | 0.2055 (10) | Ni3-N4 | 0.2064 (12) |
| Ni1-N2 | 0.2065 (12) | Ni3-N3 | 0.2094 (12) |
| Ni1-O8 | 0.2080 (9) | Ni3-O12 ^{a)} | 0.2071 (9) |

a) Symmetry code: $-x, -y, -z$.

ϵ -[Mo₈O₂₆]⁴⁻ consists of six MoO₅ square pyramids and two MoO₆ octahedra^[3]. The structure of the ξ -[Mo₈O₂₆]⁴⁻ isomer also differs from that of (α - γ)- or (β - γ)-[Mo₈O₂₆]⁴⁻ proposed by Klemperer and Shum^[10], which has not been synthesized as yet. Although the ξ -octamolybdate and (α - γ)- or (β - γ)-molybdate are all composed of four MoO₆ octahedra and four MoO₅ trigonal bipyramids, arrangements of the polyhedra in these isomers are different. In (α - γ)- or (β - γ)-isomers, the Mo₆O₆ ring contains four octahedral and two trigonal-bipyramidal Mo^{VI} atoms and there are two edge-shared MoO₅ trigonal bipyramids in the cavity enclosed by polyhedra in the ring. More specifically, ξ -[Mo₈O₂₆]⁴⁻ contains six O(μ_3), six O(μ_2) and fourteen O(t) atoms, while (α - γ)- or (β - γ)-[Mo₈O₂₆]⁴⁻ contains two O(μ_4), two O(μ_3), eight O(μ_2) and fourteen O(t) atoms.

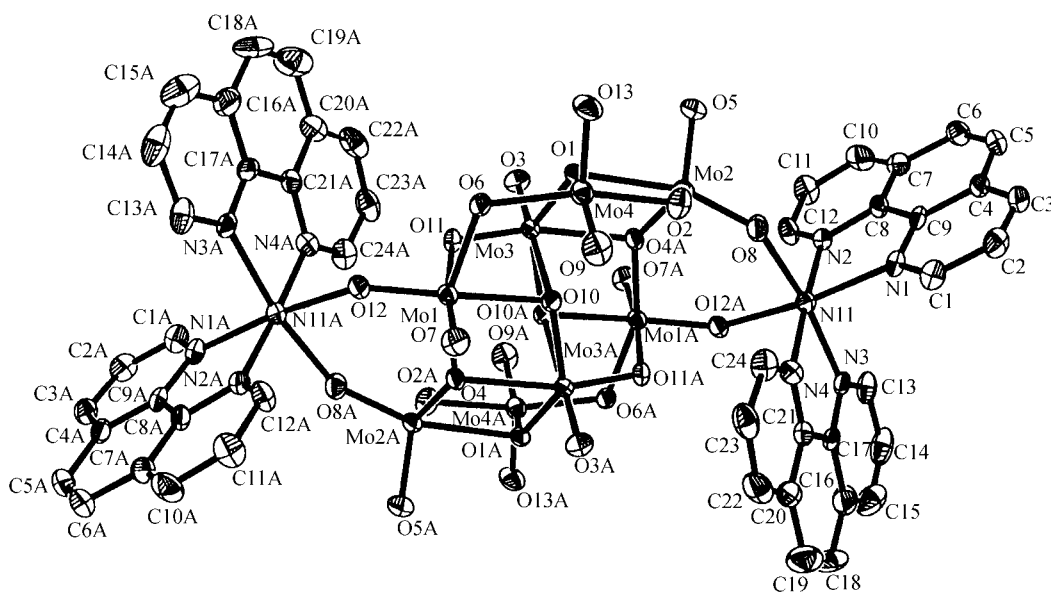


Fig. 1. Molecular drawing of [(Ni(phen)₂)₂(Mo₈O₂₆)] (50% displacement ellipsoids).

Table 3 Selected bond angles / (°)

| | | | |
|---|-----------|---------------------------|----------|
| O7-Mo1-O12 | 104.2 (5) | O7-Mo1-O6 | 99.9(5) |
| O12-Mo1-O6 | 106.9 (4) | O7-Mo1-O4 | 94.4(4) |
| O12-Mo1-O4 | 93.4 (4) | O6-Mo1-O4 | 151.1(4) |
| O7-Mo1-O10 | 99.0 (4) | O12-Mo1-O10 | 153.0(4) |
| O6-Mo1-O10 | 80.6 (3) | O4-Mo1-O10 | 72.3(3) |
| O7-Mo1-O11 | 171.9 (4) | O12-Mo1-O11 | 82.5(4) |
| O6-Mo1-O11 | 80.8 (4) | O4-Mo1-O11 | 81.7(3) |
| O10-Mo1-O11 | 73.1 (3) | O5-Mo2-O8 | 105.8(5) |
| O5-Mo2-O2 | 113.7 (5) | O8-Mo2-O2 | 101.8(5) |
| O5-Mo2-O4 ^{a)} | 113.4 (4) | O8-Mo2-O4 ^{a)} | 94.1(4) |
| O2-Mo2-O4 ^{a)} | 123.2 (4) | O5-Mo2-O1 | 91.4(4) |
| O8-Mo2-O1 | 161.6 (4) | O2-Mo2-O1 | 76.4(4) |
| O1-Mo2-O4 ^{a)} | 72.6 (3) | O3-Mo3-O11 | 104.6(5) |
| O3-Mo3-O1 | 105.3 (4) | O11-Mo3-O1 | 102.8(4) |
| O3-Mo3-O10 ^{a)} | 103.9 (4) | O11-Mo3-O10 ^{a)} | 99.6(4) |
| O1-Mo3-O10 ^{a)} | 137.0 (4) | O3-Mo3-O4 ^{a)} | 94.4(4) |
| O11-Mo3-O4 ^{a)} | 160.9 (4) | O1-Mo3-O4 ^{a)} | 73.7(3) |
| O4 ^{a)} -Mo3-O10 ^{a)} | 73.2 (3) | O9-Mo4-O13 | 105.5(6) |
| O9-Mo4-O6 | 96.9 (5) | O13-Mo4-O6 | 100.4(4) |
| O9-Mo4-O2 | 93.3 (5) | O13-Mo4-O2 | 99.9(5) |
| O6-Mo4-O2 | 153.9 (4) | O9-Mo4-O1 | 152.1(5) |
| O13-Mo4-O1 | 101.3 (4) | O6-Mo4-O1 | 85.7(4) |
| O2-Mo4-O1 | 74.3 (4) | N1-Ni1-N4 | 98.9(4) |
| N1-Ni1-N2 | 80.8 (4) | N4-Ni1-N2 | 177.2(5) |
| N1-Ni1-O12 ^{a)} | 170.6 (4) | N4-Ni1-O12 ^{a)} | 90.2(4) |
| N2-Ni1-O12 ^{a)} | 90.2 (4) | N1-Ni1-O8 | 89.3(4) |
| N4-Ni1-O8 | 91.2 (4) | N2-Ni1-O8 | 91.5(4) |
| O12 ^{a)} -Ni1-O8 | 88.3 (4) | N1-Ni1-N3 | 97.4(4) |
| N4-Ni1-N3 | 81.1 (5) | N2-Ni1-N3 | 96.1(5) |
| O12 ^{a)} -Ni1-N3 | 86.1 (4) | O8-Ni1-N3 | 170.6(4) |

a) Symmetry code: $-x, -y, -z$.

Each ξ -[Mo₈O₂₆]⁴⁻ unit is bonded to two [Ni(phen)₂]²⁺ units through terminal oxo groups of octahedral and trigonal-bipyramidal Mo sites in the Mo₆O₆ ring with Ni-O distances of 0.2071(9) and 0.2080(9) nm. Since the terminal oxo groups of fully oxidized polyoxomolybdate (all Mo sites in the VI oxidation state) are non-basic and unreactive, the formation of compound **1** indicates the oxophilicity of the [Ni(phen)₂]²⁺ group and the structural flexibility of the octamolybdate core in adopting the ξ -structure. In the [Ni(phen)₂]²⁺ unit, Ni is coordinated to four N atoms of two 1,10-phenanthroline ligands besides two terminal oxygen atoms of the octamolybdate cluster, forming a distorted octahedron with one relatively long Ni-N distance of 0.2094(12) nm and three Ni-N distances in the range of 0.2055(10)—0.2065(12) nm. Compound **1** possesses three kinds of Mo-O bonds: Mo-O(t), Mo-O(μ_2) and Mo-O(μ_3) bonds. Table 4 gives bond length ranges of three types of Mo-O bonds and Mo-O average bond lengths in the coordination polyhedra of Mo atoms. It can be seen from table 4 that Mo-O average bond lengths (0.1975 and 0.1995 nm, respectively) of hexa-coordinated Mo1 and Mo3 are much longer than those (0.1877 and 0.1903 nm) of penta-

coordinated Mo2 and Mo4. However, Mo-O average bond lengths of the penta-coordinated Mo itself are very similar to each other, and it is also the same case for hexa-coordinated Mo. It is found for Mo2, Mo3 and Mo4 coordination polyhedra that Mo-O distances increase with increasing coordination number of oxygen, i. e. $\text{Mo-O}(t) < \text{Mo-O}(\mu_2) < \text{Mo-O}(\mu_3)$, while for Mo1 site this trend is not completely met. For example, the Mo(1)-O(11)(μ_2) bond length (0.2341(10) nm) is evidently longer than the bond lengths of Mo1-O4(μ_3)(0.2032(8) nm) and Mo1-O10 (μ_3) (0.2146(8) nm).

Table 4 Bond length ranges of three types of Mo-O bonds and average Mo-O bond lengths of each Mo atom in $[\{\text{Ni}(\text{phen})_2\}_2(\text{Mo}_8\text{O}_{26})]/\text{nm}$

| Bond length ranges | Mo-O(t) | Mo-O(μ_2) | | Mo-O (μ_3) |
|---------------------------|-----------------------|----------------------|--------|---------------------|
| | 0.1685(10)—0.1711(11) | 0.1731(9)—0.2341(10) | | 0.1892(8)—0.2529(8) |
| Average Mo-O bond lengths | Mo1-O | Mo2-O | Mo3-O | Mo4-O |
| | 0.1975 | 0.1877 | 0.1995 | 0.1903 |

2.3 Investigation of electronic structure

Electronic structure of compound **1** has been performed by means of EHMO method^[11]. The fractional atomic coordinates obtained through crystal structure determination are transformed into Cartesian coordinates. The parameters of Mo and Ni atoms used in EHMO calculation are taken from the literature^[12], and other atomic parameters are usual.

Compound **1** has 124 atoms. The total number of valent molecular orbitals is 450, in which 244 are occupied ones. Total energy of the system is -9088.45 eV. The energy of the highest occupied molecular orbital (HOMO) calculated is -10.5411 eV and that of lowest unoccupied molecular orbital (LUMO) is -10.0016 eV. The energy gap between HOMO and LUMO is 0.5395 eV. Table 5 gives the levels and compositions near frontier molecular orbital.

The composition for each molecular orbital is divided into three parts: eight Mo atoms, 26 O atoms and two Ni(phen)₂ units. It can be seen from table 5 that HOMO consists of two $[\text{Ni}(\text{phen})_2]^{2+}$ (86.44%) and cluster skeleton $[\text{Mo}_8\text{O}_{26}]^{4-}$ (13.56%). The frontier molecular orbitals mainly comprise molecular orbitals of two $[\text{Ni}(\text{phen})_2]^{2+}$. It is known from wave function analysis that first unoccupied d orbital energy level of Mo atom is -9.3712 eV (No. 253 orbital), which can accept charges transferred from bridge oxygen atoms. This is in agreement with presence of O→Mo charge transfer transition in electronic absorption spectra of compound **1**.

The charge and bond order distribution of cluster skeleton $[\text{Mo}_8\text{O}_{26}]^{4-}$ are shown in fig. 2. In cluster skeleton $[\text{Mo}_8\text{O}_{26}]^{4-}$, average electronic configuration of eight Mo atoms obtained from calculation is $4d^{1.37-1.42} 5s^{0.28} 5p^{0.55}$. There are four Mo atoms with five coordinations and four Mo atoms with six coordinations in eight Mo atoms. Difference of d orbital electron between the two kinds of Mo is very slight (only 0.05e). Average net charge on ten O(t) atoms is -1.38 e, and the charges on ten O(μ_2) and six O(μ_3) are -1.260 e and -1.200 e, respectively. The charges of three kinds of oxygen atoms partly transferred into empty d orbitals of Mo atoms, resulting in that range of the net charge of Mo atom is between $+3.751$ e — $+3.806$ e.

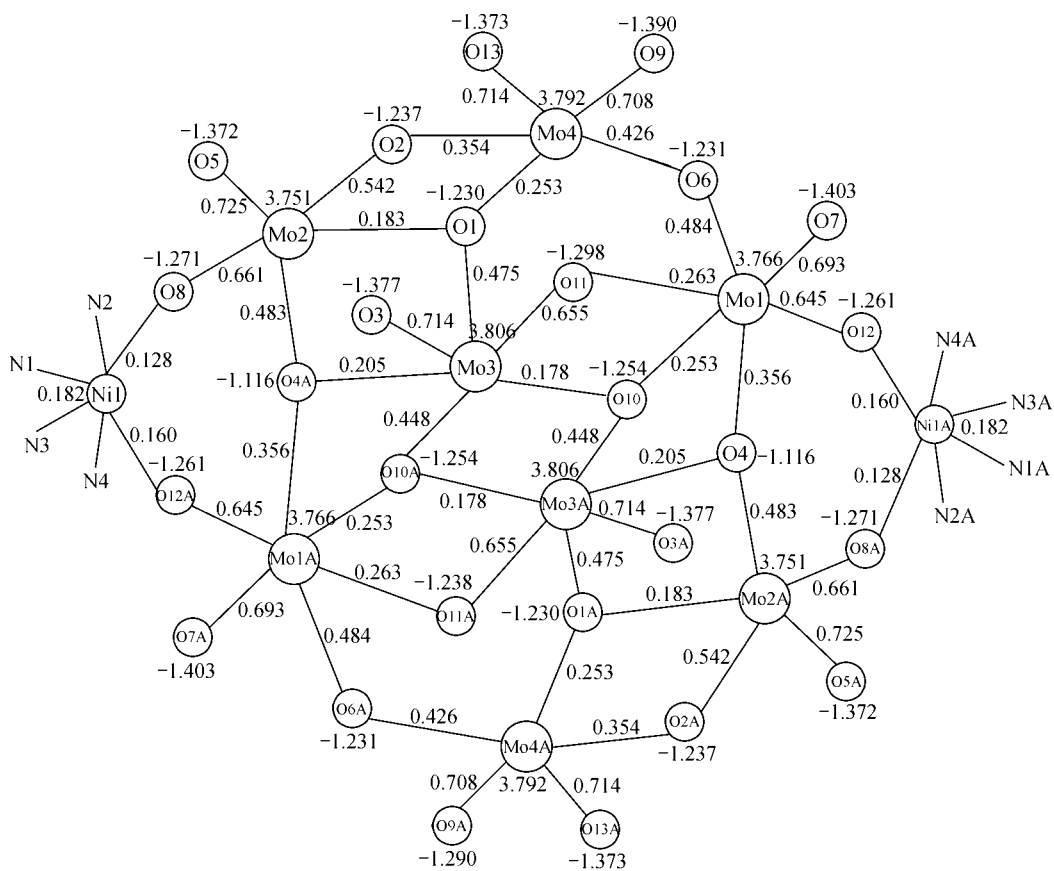


Fig. 2. Bond orders and charge distribution in $[\text{Mo}_8\text{O}_{26}]^{4-}$ of $[(\text{Ni}(\text{phen})_2)_2] (\text{Mo}_8\text{O}_{26})^{4-}$.

Table 5 Levels and compositions near frontier molecular orbitals

| No. | Energy level/eV | 8Mo | 26O | Ni(phen) ₂ | Ni(phen) ₂ | % |
|-----|-----------------|-------|-------|-----------------------|-----------------------|------|
| 254 | -9.3562 | 63.99 | 11.02 | 12.50 | 12.50 | 1.18 |
| 253 | -9.3712 | 86.69 | 12.77 | 0.27 | 0.27 | 1.16 |
| 252 | -9.4508 | 0.10 | 0.02 | 49.94 | 49.94 | 1.24 |
| 251 | -9.4508 | 0.13 | 0.03 | 49.92 | 49.92 | 1.24 |
| 250 | -9.6344 | 0.35 | 0.22 | 49.71 | 49.71 | 1.24 |
| 249 | -9.6346 | 0.36 | 0.23 | 49.71 | 49.71 | 1.24 |
| 248 | -9.6942 | 0.06 | 0.01 | 49.96 | 49.96 | 1.24 |
| 247 | -9.6942 | 0.07 | 0.01 | 49.96 | 49.96 | 1.24 |
| 246 | -10.0008 | 1.99 | 4.76 | 46.62 | 46.62 | 1.34 |
| 245 | -10.0016 | 2.14 | 4.74 | 46.56 | 46.56 | 1.34 |
| 244 | -10.5411 | 1.79 | 11.77 | 43.22 | 43.22 | 1.29 |
| 243 | -10.5412 | 1.80 | 11.77 | 43.21 | 43.21 | 1.29 |
| 242 | -12.2804 | 0.07 | 0.69 | 49.62 | 49.62 | 0.97 |
| 241 | -12.2804 | 0.07 | 0.70 | 49.61 | 49.61 | 0.97 |
| 240 | -12.3072 | 0.02 | 0.30 | 49.84 | 49.84 | 0.92 |
| 239 | -12.3072 | 0.02 | 0.30 | 49.84 | 49.84 | 0.92 |
| 238 | -12.3344 | 0.01 | 0.21 | 49.89 | 49.89 | 0.91 |
| 237 | -12.3344 | 0.01 | 0.21 | 49.89 | 49.89 | 0.91 |

As to bond order, average bond order of Mo-O(t) in $[\text{Mo}_8\text{O}_{26}]^{4-}$ is 0.711, which possesses double bond character. The bond order of Mo-O(μ_2) is divided into two classes: one is that both side Mo-O(μ_2) bond orders of linking one and the same O(μ_2) are basically equal and possess single bond character. For examples, two bond orders of Mo1-O6-Mo4 are 0.484 and 0.426, respectively. The other class of two Mo-O(μ_2) bond orders linking the same O(μ_2) is obviously different, in which the bigger bond order possesses double bond character, for example, bond order of Mo3-O11(0.655) in Mo3-O11-Mo1 is just in this case, while smaller bond order, Mo1-O11 (0.263), displays coordination bond character. This is in agreement with relatively shorter Mo3-O11 bond length (0.1734(8) nm) and longer Mo1-O11 bond length (0.2341(10) nm) obtained from single crystal structure determination of the compound. The latter bond is formed by O11 atom providing lone pair for Mo1 d empty orbital. Bond orders of Mo1A-O12A in Mo1A-O12A-Ni1 and Mo2-O8 in Mo2-O8-Ni1 are 0.645 and 0.661, respectively. Their bond lengths are respectively 0.1740(9) and 0.1731(9) nm, possessing double bond character. While bond orders of Ni1-O12A and Ni1-O8 are respectively 0.160 and 0.128, and the bond lengths are respectively 0.2071(9) and 0.2080(9) nm, indicating coordination bond character. It is deduced from this that forming process of the compound **1** is probably that cluster skeleton anion $[\text{Mo}_8\text{O}_{26}]^{4-}$ and coordination cation $[\text{Ni}(\text{phen})_2]^{2+}$ firstly form, respectively, then four terminal O(t) atoms in $[\text{Mo}_8\text{O}_{26}]^{4-}$ provide their lone pairs for two Ni atoms in $[\text{Ni}(\text{phen})_2]^{2+}$ units, forming coordination bonds.

The average bond orders of Mo-O(t), Mo-O(μ_2) and Mo-O(μ_3) are 0.711, 0.454 and 0.315, respectively, which are in agreement with corresponding characteristic absorption peaks (945, 885 and 705 cm^{-1}) of infrared spectra of the compound.

To date, the six kinds of $[\text{Mo}_8\text{O}_{26}]^{4-}$ isomers have been synthesized, but their functional performances were rarely reported. At present, nonlinear optical properties of these isomers are being investigated in our laboratory.

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