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SYNTHESIS AND CHARACTERIZATION OF A SANDWICH-TYPE CERIUM (IV) COMPLEX DERIVED FROM MONOLACUNARY DAWSON 2-MOLYBDO-15-TUNGSTO-2-PHOSPHATE

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ABSTRACT. The reaction of monolacunary Dawson 2-molybdo-15-tungsto-2-phosphate, i.e. $[1,2\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ with $Ce(SO_4)_2$ in aqueous solution results in the formation of a new polyoxometalate complex, with the stoichiometry metal:ligand = 1:2. The new complex was isolated as potassium salt, i.e. $K_{16}[Ce(P_2Mo_2W_{15}O_{61})_2]\cdot 34H_2O$. The molecular formula was determined by elemental and thermogravimetric analysis. UV-Vis, FT-IR and ^{31}P-NMR spectroscopy were used to characterize the new compound. Ion-exchange chromatography provided evidence for covalent, inner-sphere bonding of cerium (IV) to the monolacunary $[1,2\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ heteropolyoxometalate anion. The investigation results strongly suggest a sandwich-type structure with the cerium atom coordinated by two monolacunary Dawson anions.

Keywords: *polyoxometalate, heteropolyoxometalate, cerium, 2-molybdo-15-tungsto-2-phosphate, ^{31}P-NMR*

INTRODUCTION

Polyoxometalates (POMs) are discrete molecular metal-oxygen clusters with unrivaled versatility and structural variety [1-4], and therefore they show a multitude of properties, which has led to applications, in many fields such as catalysis [5], molecular conduction [7-9], magnetism [10], medicine [11,12], luminescence [13], as well as materials science [14].

The synthesis of POMs is mostly rather simple and straightforward, once the proper reactions conditions have been identified. However, the mechanism of formation of POMs, usually described as self-assembly, is not yet completely understood. Therefore, the design of novel POMs remains a challenge for synthetic chemists.

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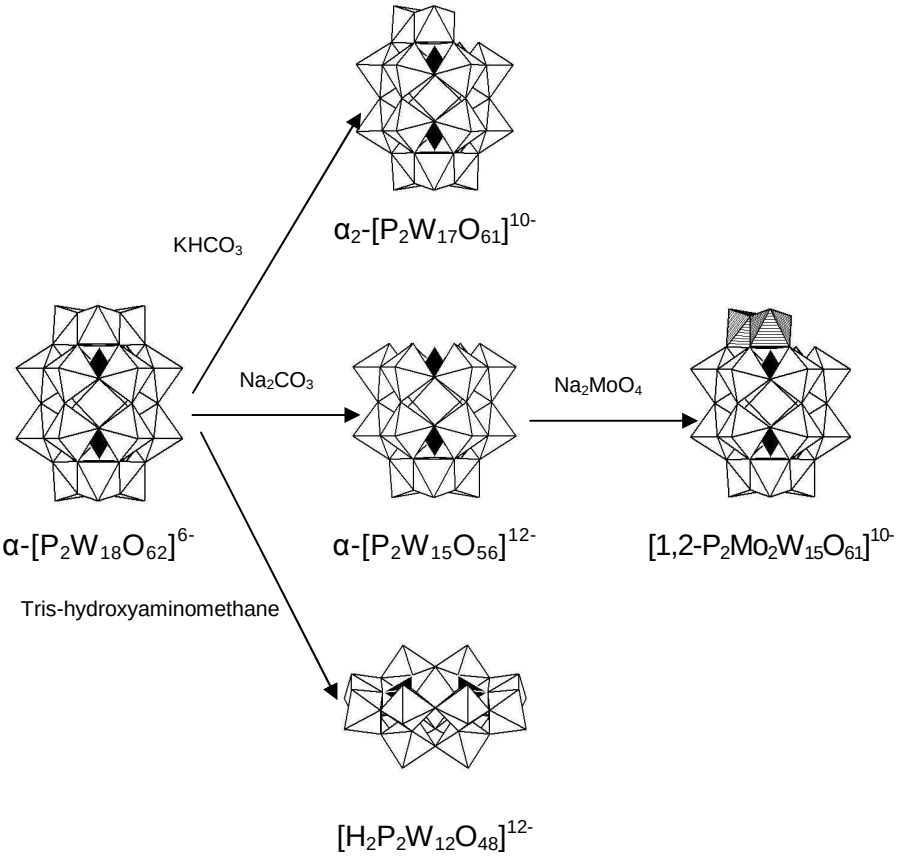
The most rational approach for the synthesis of POMs involves the use of lacunary species. Reaction of a stable, lacunary POM with transition metal or lanthanide ions leads to a product in which the polyoxometalate framework is not modified.

For instance, under hydrolytic conditions, a cluster such as the well-known α-$[P_2W_{18}O_{62}]^{6-}$ Dawson polyoxotungstate may generate lacunary derivatives with one, three or more lacunary sites (Scheme 1) [15-17].



Scheme 1

The reaction of Dawson trilacunary α-pentadecatungsto-diphosphate with molybdate, carried out in mild conditions allows the selective addition of two molybdenum atoms in an apical. It is possible to refill the vacancy of the resulting $[1,2\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ monolacunary Dawson anion, with transition metal cations. Such complexes with first row transition metal cation exhibit interesting electrocatalytic properties [18-20].

On the other hand, two monolacunary polyoxometalate units may coordinate large central metal ions with high coordination numbers, such as lanthanides or actinides [21-29].

Herein we report the synthesis and characterization of a new complex of Ce(IV) with the $[1,2\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ monolacunary Dawson polyoxometalate, isolated as aqueous soluble potassium salt $K_{16}[Ce(P_2Mo_2W_{15}O_{61})_2]\cdot 34H_2O$ (**4**). The complex **4** was characterized by elemental and thermogravimetric analysis, UV-Vis, FT-IR and ^{31}P-NMR spectroscopy, as well as by ion-exchange chromatography.

RESULTS AND DISCUSSION

The Ce(IV) complex was synthesized in aqueous solution by reacting the potassium salt of the monolacunary Dawson polyoxometalate $K_{10}[1,2\text{-}P_2Mo_2W_{15}O_{61}]\cdot 18H_2O$ (**3**) with cerium (IV) sulfate. In order to avoid the migration of molybdenum atoms which may give numerous isomers the synthesis must be performed in acidic solution without heating.

Elemental analysis of the cerium (IV) polyoxometalate complex is consistent with the suggested formula.

The thermal stability of **4** was investigated by TG-DTG-DTA. The weight loss in the 25 - 170°C range corresponds to 34 lattice water molecules. The loss of water by heating proceeds in two steps, as observed on the DTG curve. The dehydration process is accompanied by an endothermal process between ~25 - 170°C, as observed on the DTA curve (Figure 1). According to the literature, the first exothermic peak of DTA curve, which usually occurs 20-30°C after the temperature of the polyoxometalate decomposition [30, 31], is regarded as the thermal stability sign of polyoxometalates [32]. For **4**, the first exothermic peak appeared at 489°C, indicating a good thermal stability of the complex. The second exothermic peak at 560°C may be assigned to some phase transitions of the resulting oxides.

When a solution of **4** was loaded onto the sodium form (*P*-$SO_3^-Na^+$) of the cation-exchange column, no retention of the Ce(IV) complex was observed. The FT-IR spectrum of the eluant confirmed the integrity of the eluted parent complex, **4**. In a second series of experiments, a sample of **4** was loaded onto an anion-exchange column in its Cl form, *P*-$NR_3^+Cl^-$. In this case the Ce(IV) polyoxometalate complex was retained on the column. Control experiments were carried out with aqueous solutions of $Ce(SO_4)_2$. As expected, the cerium cations were retained on the cation-exchange column but passed through the anion-exchange column. Consequently, these simple ion-exchange experiments provide good evidence for inner-sphere bonding of the Ce(IV) cations to **3** [33].

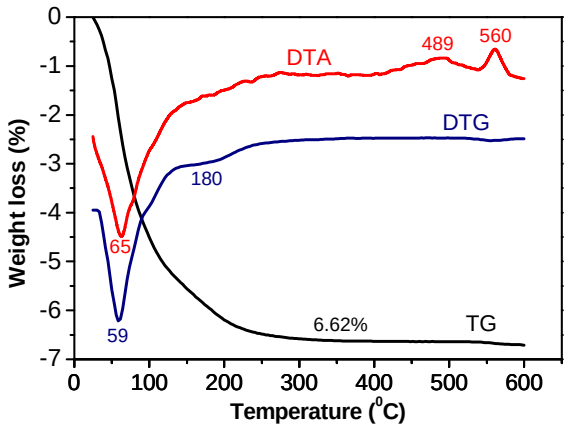


Figure 1. Thermogravimetric and thermodifferential curves of **4**.

UV spectra of the ligand (**3**) and complex (**4**) (Figure 2) show two characteristic absorption bands assigned to the dπ-pπ charge transfer transitions M←O_t (v_2) and M←O_b (v_1) respectively (M is Mo or W; O_t is a terminal oxygen and O_b is a bridging oxygen) [34]. The v_1 band shows a significant red shift in **4** when compared to the monolacunary Dawson ligand. On the other hand, the molar absorption coefficient of the v_2 band, which is proportional to the number of addenda atoms, is almost twice greater in complexes than in the ligand ($\varepsilon \approx 3.46 \times 10^5$ *vs.* 1.76×10^5 L mol^{-1} cm^{-1}), indicating the existence of two monolacunary ligand units in **4** [35].

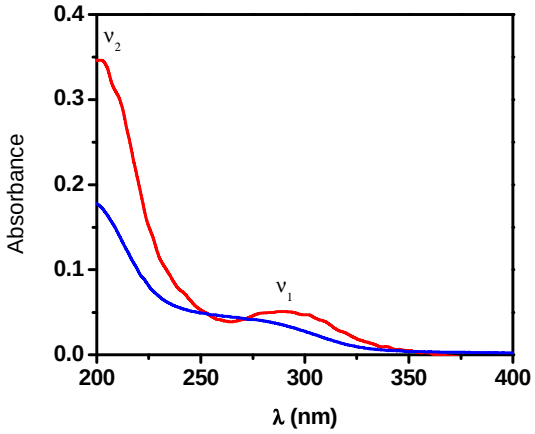


Figure 2. UV electronic spectra of **3** (blue) and **4** (red), recorded in 10^{-6} M aqueous solution.

The ^{31}P NMR spectrum of **4** in D_2O (Figure 3) showed a clean two-line spectrum with signals at -8.27 and -13.22 ppm, confirming its purity and single-product nature. The low-field peak has been assigned to the P(1) phosphorous atom close to the coordination site of Ce(IV) [36-38]. It is easily seen that, the chemical shift of the P2 (remote phosphorus) resonance does not vary greatly in going from the lacunary structure to the Ce(IV) complex. The chemical shift of the P1 (near phosphorus atom) resonance, however, experiences pronounced up field shift upon complexation with Ce(IV).

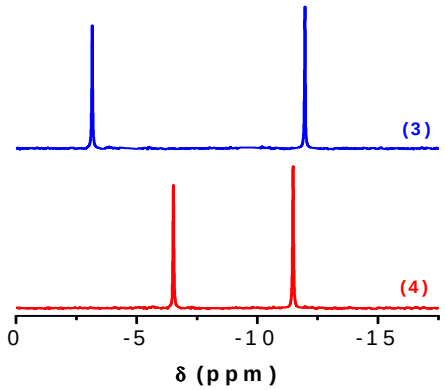


Figure 3. ^{31}P NMR spectrum of **3** and **4** recorded in D_2O

The IR spectrum of **4** (Figure 4) is closely related to that of the parent Dawson monolacunary ligand **3** in the 400-1200 cm^{-1} range, suggesting that the polyoxometalate framework is maintained.

It is well known that the most characteristic changes in the IR spectra of the molybdotungstophosphates, are observed for the P-O stretching vibrations band in the 1000-1200 cm^{-1} range, when comparing the saturated species, lacunary derivatives and their complexes [39]. For instance, when a transition metal cation is added into the vacancy of a monolacunary Dawson polyoxometalate, the whole symmetry of the anion is restored, at least as far as IR spectra are concerned, and the spectra of the transition metal derivatives are very close to the spectrum of complete Dawson anion [36]. A different situation is observed in the case of complexes of monolacunary Dawson polyoxometalate with larger cations (i.e. lanthanides or actinides) which cannot fill the vacancy and therefore coordinate only through the four oxygen atoms that surrounded the addendum vacancy. The IR spectra of such complexes are very close to the spectra of the lacunary Dawson polyoxometalates [27].

As expected, in the spectra of **3** and **4**, the band assigned to P-O asymmetric stretching vibrations is split into three components (1086, 1051 and 1016 cm^{-1}, respectively).

The bands in the 1000-700 cm^{-1} range were assigned to the asymmetric stretching vibrations of the bridges (M-O_b-M) and of the terminal bonds (M-O_t) [40].

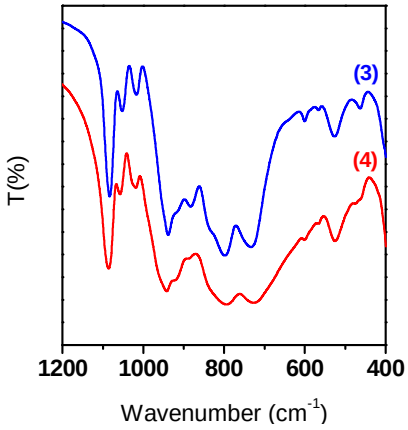


Figure 4. FT-IR spectra of **3** and **4**, recorded in KBr pellets.

On the basis of the analytical and spectral data, a sandwich-type structure is proposed for the Ce(IV) complex **4**. In this structure, the Ce(IV) ion is in a square antiprismatic environment with eight oxygen atoms, four from each of the two monolacunary Dawson ligands, as shown in figure 5.

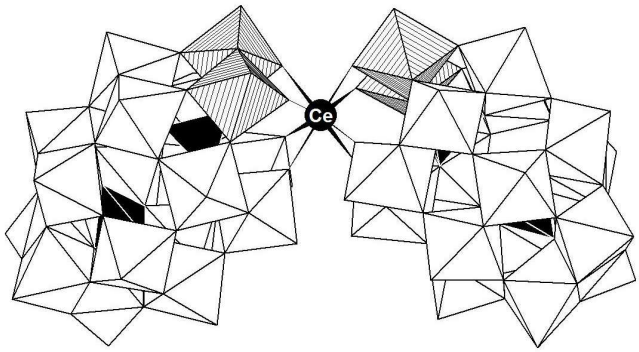


Figure 5. Proposed structure of the polyoxometalate complex **4**.

CONCLUSIONS

A **$K_{16}[Ce(P_2Mo_2W_{15}O_{61})_2]\cdot 34H_2O$** complex was prepared by the reaction of $Ce(SO_4)_2$ with the potassium salt of monolacunary Dawson 2-molybdo-15-tungsto-2-phosphate **$K_{10}[1,2\text{-}P_2Mo_2W_{15}O_{61}]\cdot 18H_2O$** after establishing optimal synthesis conditions. Analytical and spectroscopic data, as well as ion exchange chromatography experiments suggest a sandwich-type structure for the complex, in which the cerium ion is coordinated by four oxygen atoms of the two monolacunary Dawson anions.

EXPERIMENTAL SECTION

Materials

Reagent grade chemicals were used and all syntheses and investigations were carried out in distilled water.

The Dawson precursors $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot xH_2O$ (**1**), $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 21H_2O$ (**2**) and $K_{10}[1,2\text{-}P_2Mo_2W_{15}O_{61}]\cdot 18H_2O$ (**3**) were prepared according to the literature [41-43].

*Synthesis of $K_{16}[Ce(P_2Mo_2W_{15}O_{61})_2]\cdot 34H_2O$ (**4**)*

A sample of $Ce(SO_4)_2\cdot 4H_2O$ (0.202 g, 0.5 mmol) was dissolved in water (10 mL) and added dropwise, while stirring, to a solution of $K_{10}[1,2\text{-}P_2Mo_2W_{15}O_{61}]\cdot 18H_2O$ (5 g, 1 mmol) dissolved in 110 mL of molar acetic acid – lithium acetate buffer (pH=3.5). The resulting yellow solution was left under stirring for 30 min and then 50 mL saturated solution of KCl was added. A yellow precipitate appeared immediately. After 10 min the resulting yellow precipitate was filtered on a sintered glass frit, washed with ethanol and diethyl ether, and dried in air.

Calcd. for $K_{16}[Ce(P_2Mo_2W_{15}O_{61})_2]\cdot 34H_2O$ P: 1.32; K: 6.69; Mo: 4.10; Ce: 1.50; W: 58.97. H_2O 6.55. Found: P: 1.28; K: 6.72; Mo: 4.02; Ce: 1.44; W: 58,88. H_2O 6.62. FT-IR (polyoxometalate region, cm^{-1}): 1086, 1059, 1018, 943, 924, 889, 796, 725, 602, 565, 526, 474.

Methods

The contents of cerium, phosphorous, molybdenum, and tungsten were determined by inductively coupled plasma atomic emission spectroscopy on a Rigaku Spectro CIROS^{CCD} spectrometer. Potassium was determined by FEP with an Eppendorf flame photometer. The water content was thermogravimetrically determined, by means of a METTLER-TOLEDO TG/SDTA 851 thermogravimeter (Pt crucible, 20 mL/min nitrogen flow, 5ºC/min heating rate).

A JASCO 610 FTIR spectrophotometer was used to record the FTIR absorption spectra in KBr pellets.

UV-Vis spectra were recorded on a Shimadzu UV-3101PC instrument using Teflon-stoppered quartz cells with a path length of 1 cm.

^{31}P-NMR spectra were recorded at 101.2561380 MHz using an ARX 250 spectrometer. Chemical shifts are reported in ppm using D_3PO_4 as external reference.

For the ion-exchange chromathography experiments, degassed water (50 mL) was added to the strongly acidic macroreticular resin (10 g), Vionit CS3 (H~ form; *P*-SO_3H where *P* = macroreticular polymer). The resin was repeatedly washed in water until the aqueous phase was clear and colourless. The resin was then packed into a column (27 cm x 1 cm; length x diameter) and a solution of 4% NaOH was eluted through the column. The resulting *P*-SO_3Na column was washed five times with distilled water (50 ml). A solution of **4** (0.5 g) in H_2O (10 ml), was loaded onto the column. The eluant was collected and the solvent removed by evaporation. The FT-IR spectrum of the collected Ce(IV) complex appeared unchanged when compared with the FT-IR spectrum of the complex before elution. An anion exchange column of identical size was packed with strongly basic resin, Amberlyst A-27 (C1 form; *P*-$NR_3^+Cl^-$). A sample of **4** was loaded onto the column in a manner similar to that described for the cation exchange resin. All samples were retained by the resin, in the upper half of the column.

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REFERENCES

1. M.T. Pope, A. Müller (Eds.), "Polyoxometalates: From Platonic Solid to Antiretroviral Activity", Kluwer Academic Publishers, Dordrecht, **1994**.
2. M.T. Pope, A. Müller (Eds.), "Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications", Kluwer Academic Publishers, Dordrecht, **2001**.
3. T. Yamase, M.T. Pope (Eds.), "Polyoxometalate Chemistry for Nano-Composite Design", Kluwer Academic Publishers, Dordrecht, **2002**.
4. J.J. Borrás-Almenar, E. Coronado, A. Müller, M.T. Pope (Eds.), "Polyoxometalate Molecular Science", Kluwer Academic Publishers, Dordrecht, **2004**.
5. M. Misono, *Chemical Communications*, **2001**, 1141.
6. I.V. Kozhevnikov, "Catalysts for fine chemical synthesis. Vol. 2. Catalysis by polyoxometalates.", Wiley & Sons, Chichester, England, **2002**.

7. E. Coronado, C. Giménez-Saiz, C.J. Gómez-García, S.C. Capelli, *Angewandte Chemie, International Edition,* **2004**, *43*, 3022.
8. E. Coronado, P. Day, *Chemical Reviews*, **2004**, *104*, 5419.
9. E. Coronado, C. Giménez-Saiz, C.J. Gómez-García, *Coordination Chemistry Reviews*, **2005**, *249*, 1776.
10. E. Coronado, P. Delhaes, D. Gatteschi, J.S. Miller, "Molecular Magnetism: From Molecular Assemblies to the Devices.", Kluwer Academic Publishers, vol. E-321, **1996**.
11. J.T. Rhule, C.L. Hill, D.A. Judd, *Chemical Review*, **1998**, *98*, 327.
12. T. Yamase, *Journal of Materials Chemistry*, **2005**, *15*, 4773.
13. T. Yamase, *Chemical Review*, **1998**, *98*, 307.
14. D.E. Katsoulis, *Chemical Review*, **1998**, *98*, 359.
15. J.P. Ciabrini, R. Contant, J.M. Fruchart, *Polyhedron*, **1983**, *2*, 1229.
16. R. Contant, J.P. Ciabrini, *Journal of Chemical Research* (M), **1977**, 2601.
17. R. Contant, *Inorganic Synthesis*, **1990**, *27*, 104.
18. B. Keita, L. Nadjo, R. Contant, *Journal of Electroanalytical Chemistry,* **1998**, *443*, 168.
19. B. Keita, Y. Jean, B. Levy, L. Nadjo, R. Contant, *New Journal of Chemistry* **2002**, *26*, 1314.
20. B. Keita, Y.W. Lu, L. Nadjo, R. Contant, M. Abbessi, J. Canny, M. Richet, *Journal of Electroanalytical Chemistry*, **1999**, *477*, 146.
21. R.D. Peacock, T.J.R. Weakley, *Journal of the Chemical Society A,* **1971**, *A*, 1836.
22. G. Marcu, M. Rusu, A.V. Botar, *Revue Roumaine de Chimie*, **1974**, *19*, 827.
23. G. Marcu, M. Rusu, *Revue Roumaine de Chimie*, **1977**, *22*, 227.
24. G. Marcu, M. Rusu, A. Botar, *Revue Roumaine de Chimie*, **1989**, *34*, 207.
25. J. Bartis,S. Sukal, M. Dankova, E. Kraft, R. Kronzon, M. Blumenstein, L.C. Francesconi, *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry*, **1997**, 1937.
26. Q.H. Luo, R.C. Howell, M. Dankova, J. Bartis, C.W. Williams, W.D.Jr. Horrocks, V.G. Young, A.L. Rheingold, L.C. Francesconi, M.R. Antonio, *Inorganic Chemistry*, **2001**, *40*, 1894.
27. A. Ostuni, R.E. Bachman, M.T. Pope, *Journal of Cluster Science*, **2003**, *14*, 431.
28. N. Belai, M.H. Dickman, M.T. Pope, R. Contant, B. Keita, I.M. Mbomekalle, L. Nadjo, *Inorganic Chemistry*, **2005**, *44*, 169
29. C. Zhang, R.C. Howell, Q.H. Luo, H.L. Fieselmann, L.J. Todaro, L.C. Francesconi, *Inorganic Chemistry*, **2005**, *44*, 3569.
30. Q. Wu, E. Wang, J. Liu, *Polyhedron*, **1993**, *12*, 2563.
31. Z.P. Wang, J.Y. Niu, L. Xu, J. Peng, E.B. Wang, *Acta Chimica Sinica*, **1995**, *53*, 757.
32. G. Sun, J. Feng, H. Wu, F. Pei, K. Fang, H. Lei, *Journal of Magnetism and Magnetic Materials*, **2004**, 281, 405.
33. M. Pohl, D.K. Lyon, N. Mizuno, K. Nomiya, R.G. Finke, *Inorganic Chemistry*, **1995**, *34*, 1413.

34. H. So, M.T. Pope, *Inorganic Chemistry*, **1972**, *11*, 1441.
35. D. Rusu, C. Crăciun, M. Rusu, A. Pătruț, L. David, *Revue Roumaine de Chimie*, **2007**, *52*, 817.
36. M. Abbessi, R. Contant, R. Thouvenot, G. Hervé, *Inorganic Chemistry*, **1991**, *30*, 1695.
37. S.P. Harmalker, M.A. Leparulo, M.T. Pope, *Journal of American Chemical Society*, **1983,** *105*, 4286.
38. M.A. Leparulo-Loftus, M.T. Pope, *Inorganic Chemistry*, **1987**, *26*, 2112.
39. J.P. Ciabrini, R. Contant, *Journal of Chemical Research* (M), **1993**, 2720.
40. C. Rocchiccioli-Deltcheff, R. Thouvenot, *Spectrochimica Acta*, **1976**, *32A*, 587
41. C.R. Graham, R.G. Finke, *Inorganic Chemistry*, **2008**, *47*, 3679.
42. B.J. Hornstein, R.G. Finke, *Inorganic Chemistry*, **2002**, *41*, 2720.
43. M. Abbessi, R. Contant, R. Thouvenot, G. Hervé, *Inorganic Chemistry*, **1991**, *30*, 1695.