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A New Layered Compound Containing $[PMo_{12}O_{40}]^{3-}$ and Both 5- and 6-Coordinated Homoleptic (1-(2-Chloroethyl)tetrazole)Copper(II) Cations

Arno F. Stassen[1], **Eugenia Martínez Ferrero**[2], **Carlos Giménez-Saiz**[2], **Eugenio Coronado**[2], **Jaap G. Haasnoot**[1,*], and **Jan Reedijk**[1]

[1] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[2] Instituto de Ciencia Molecular, Universidad de Valencia, 46100 Burjassot, Spain

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Summary. The synthesis, crystal structure and physical properties of the complex obtained from the reaction between the polyoxometalate anion $[PMo_{12}O_{40}]^{3-}$, copper(II) and the ligand 1-(2-chloroethyl)tetrazole (*teec*) are described. This compound has been synthesized as a model for designing materials containing both magnetic polyoxometalate anions and iron(II) spin-crossover cations.

The compound, with formula $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$, consists of alternating layers of polyoxometalates and cationic complexes. Both, five and six coordinated Cu(II) ions are present, each positioned in different layers. Despite these layers having a similar width, the layer of pentacoordinated Cu(II) ions contains twice as many cationic complexes as the layer of hexacoordinated Cu(II) ions. This unusual coexistence of complexes with different coordination number is most likely caused by the steric hindrance induced by the bulky polyoxometalates in the layer of pentacoordinated Cu(II) which prevents the presence of a sixth *teec* ligand.

Keywords. Coordination chemistry; Heterocycles; Polyoxometalates; Structure elucidation; Tetrazole.

Introduction

The design of new hybrid materials combining two or more different properties not normally associated with a single material is a contemporary challenge in molecular chemistry. The various combinations have resulted in interesting magnetic [1–3], photophysical [4, 5] and electric [2] phenomena.

* Corresponding author. E-mail: haasnoot@chem.leidenuniv.nl

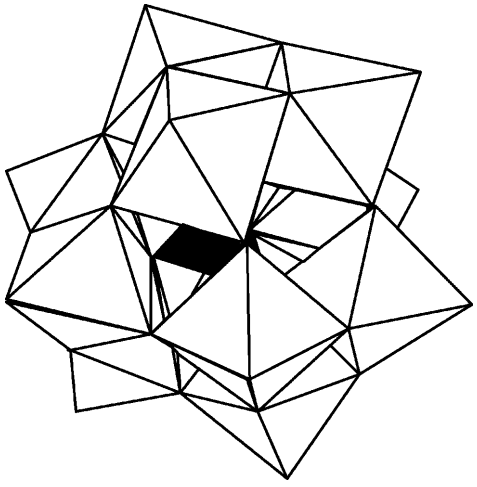

Fig. 1. Polyhedral representation of the *Keggin* polyoxometalate $[PMo_{12}O_{40}]^{3-}$

The aim of this research is to obtain model systems for coordination complexes, in which magnetic polyoxometalate anions are combined with cations undergoing a temperature-dependent spin transition. The 12-molybdophosphate anion has been chosen for this purpose. It has the well-known *Keggin* structure that consists of an arrangement of 12 MO_6 ($M = W$, Mo) octahedra sharing edges and corners surrounding a central XO_4 tetrahedron (see Fig. 1). Many different heteroatoms can occupy the central tetrahedral site (*e.g.* $X = S^{VI}$, P^V, As^V, Si^{IV}, Ge^{IV}, H_2^{2+}, B^{III}, Cr^{III}, Fe^{III}, Co^{III}, Co^{II}, Cu^{II}, Zn^{II}, ...) [6].

Polyoxometalates are widely used in chemistry [7], biology [8], physics [9] and material science [10]. In spin-crossover research, polyoxometalate anions can be of interest because of both their size and physical properties. The large size of the polyoxometalate anions can be used for synthesizing compounds, in which the spin-crossover iron(II) complexes are either positioned in two-dimensional planes, or in one-dimensional chains, i.e. by using polyoxometalates of different shape and/or charge. In this way, the elastic cooperativity required to obtain useful spin-crossover phenomena in the solid state is reduced from three dimensions to only two, or even to only one dimension. This feature should facilitate the study of cooperativity in these solids.

The combination of 1-(2-chloroethyl)tetrazole (*teec*) and copper(II) has been used, because this system [11–13] and the equivalent iron(II) spin crossover systems [14, 15] have been studied intensely over the last few years. The iron(II) complexes show a thermal spin transition at relatively high temperatures compared to other 1-alkyltetrazole compounds [16], but crystallize poorly. Therefore the copper(II) ion has been used, which has, with this ligand, proved to result in good quality single crystals.

Results and Discussion

Description of the structure

The asymmetric unit of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$ (**1**) is depicted in Fig. 2 (crystal data Table 1). The crystallographic unit cell contains two

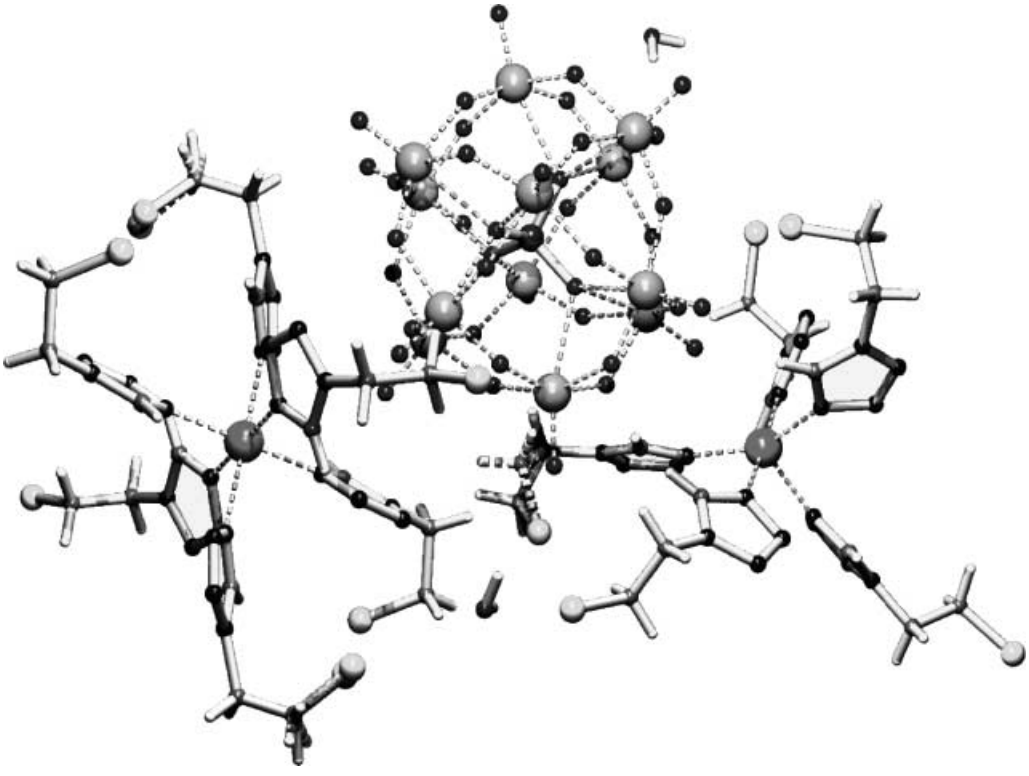

Fig. 2. Molecular structure [28, 29] of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$

$[PMo_{12}O_{40}]^{3-}$ anions, two copper(II) ions surrounded by five teec ligands, one copper(II) ion surrounded by six teec ligands and finally two water molecules. The $[Cu(teec)_6]^{2+}$ center is positioned on an inversion center (0, 1/2, 1/2), resulting in three teec ligands with unique positions, and three obtained by symmetry. One of the two $[PMo_{12}O_{40}]^{3-}$ anions and one of the five-coordinated copper(II) ions are obtained by symmetry ($-x$, $-y$, $-z$). The same occurs with the water molecules, which are equally distributed over four positions.

Compound **1** shows a layered structure with three different types of layers: layers of *Keggin* polyoxometalates (layers of type A), layers of complexes $[Cu(teec)_5]^{2+}$ (layers of type B) and layers of complexes $[Cu(teec)_6]^{2+}$ (layers of type C). These three layers are arranged in the structure following the pattern ...ABACABAC... (see Fig. 4).

The layer of $[Cu(teec)_5]^{2+}$ centers (B layer) contains twice as many copper centers as the layer of $[Cu(teec)_6]^{2+}$ (C layer), whereas the space available is not twice as large (the distance between the layers of $[PMo_{12}O_{40}]^{-3}$ anions is 14.55 Å for the C-type layers and 15.66 Å for the B-type layers).

In the layer of type B, the $[Cu(teec)_5]^{2+}$ centers (see Fig. 3, left) show one of the bond lengths (Cu(1)–N(9)) approximately 0.2 Å longer than the other four copper–nitrogen bonds. The two ligands coordinated via N(5) and N(17) are moved away from N(9), resulting in angles with N(9) of over 100°. The other two ligands make almost square angles with N(9). The angles within the distorted equatorial plane are between 87.7(5)° and 92.6(4)° (Table 2). The τ value for this

Table 1. Crystal data and structure refinement for $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$

Compound	$[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$
Compound	$Cu_3(teec)_{16}[PMo_{12}O_{40}]_2 \cdot 2H_2O$
Chemical formula	$C_{48}H_{84}N_{64}Cu_3Cl_{16}P_2Mo_{24}O_{82}$
Molecular weight	5991.97
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	11.717(4)
b, Å	12.010(17)
c, Å	30.21(3)
α, °	88.32(12)
β, °	80.93(5)
γ, °	71.40(5)
V, Å^3	3978(7)
Z	2
D_{calc}, g cm^{-3}	2.500
Absorption coefficient	2.608 mm^{-1}
Temperature	293(2) K
$F(000)$	2869.0
Crystal color, shape	Green, elongated plates
Crystal size	$0.48 \times 0.2 \times 0.05$ mm^3
Radiation, wavelength, Å	Mo Kα, 0.71069
Monochromator	Graphite
Diffractometer	Enraf Nonius CAD4
Theta range for data collection	1.37 to 24.98°
Index ranges	$0 \leq h \leq 13,\ -13 \leq k \leq 14,\ -35 \leq l \leq 35$
Reflections collected	14687
Independent reflections	13935 [R(int) = 0.0777]
Absorption correction	Psi-scan
Max. and min. transmission	0.9989 and 0.7661
Refinement method	Full-matrix-squares on F^2
Data/restrains/parameters	13935/5/1097
Goodness-of-fit on $F^2(S)$	1.058
Final R indices [I > 2sigma(I)]	$R1 = 0.0551$, $wR2 = 0.1534$
R indices (all data)	$R1 = 0.1581$, $wR2 = 0.19077$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$, e Å^{-3}	3.097, −1.719
R_{int}, R_σ	0.0777, 0.1064
Structure solution	SIR-97
Structure refinement	SHELXL-97

Calc $w = 1/[\sigma^2(F_o^2) + (0.1094P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$

complex is 0.38 [17]. This parameter reflects the degree of trigonality. For a perfectly tetragonal geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyrimidal geometry. Then, the geometry of the five-coordinated copper(II) ions can be seen as possessing a strongly distorted tetragonal-pyramidal geometry, this geometry is not common for copper(II) surrounded by monodentate tetrazole ligands. All previously published [11, 12, 18–23] structures of copper(II)

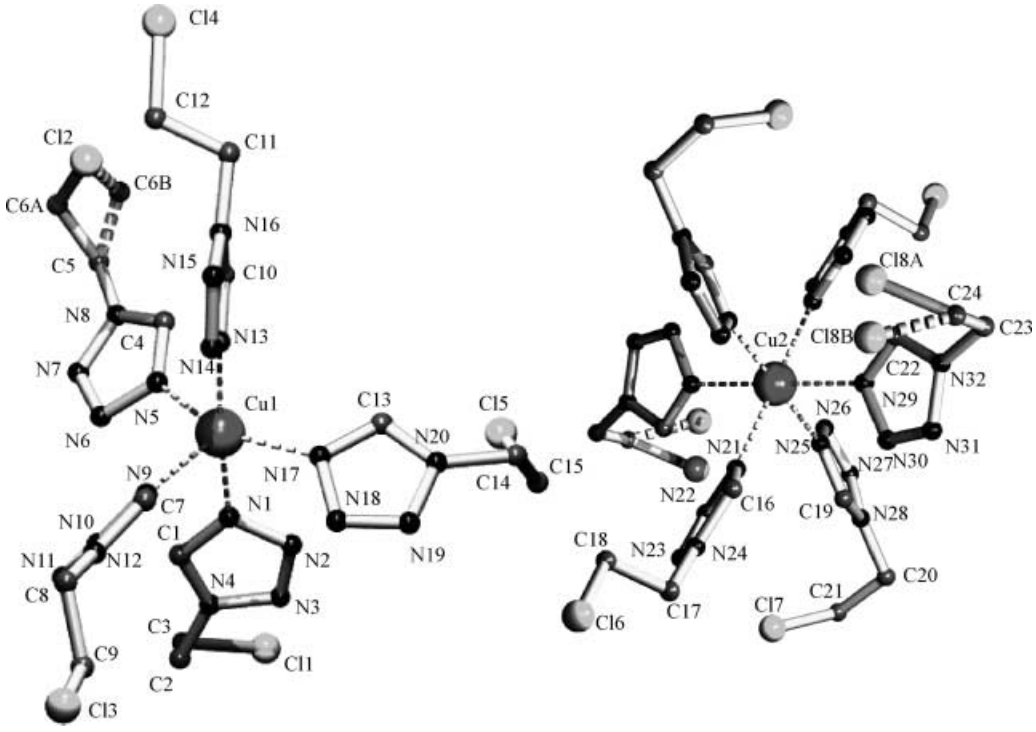

Fig. 3. Molecular structure of the copper centers; left: $[Cu(teec)_5]^{2+}$, right: $[Cu(teec)_6]^{2+}$ [28, 29]

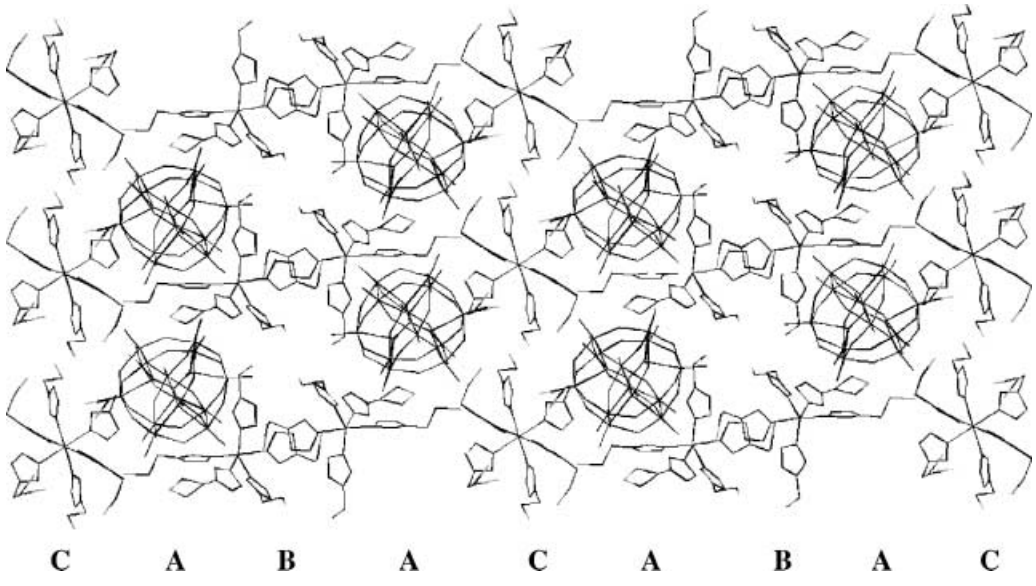

Fig. 4. Packing of the layers along the *b* axis [29]

with tetrazole ligands possess hexakis surrounded copper(II) centers of the form CuL_6 or CuL_2X_4. A closer look to the environment of Cu(1) results in the observation of a terminal oxygen atom of the polyoxometalate anion, O(20), at a distance of 3.152(10) Å of Cu(1) with an angle N(9)–Cu(1)–O(20) of 178.2(4)°, *i.e.* at a

Table 2. Selected angles (°) of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$

Atoms	Angle (°)	Atoms	Angle (°)
N21–Cu2–N25	87.5(5)	N5–Cu1–N9	108.5(4)
N21–Cu2–N29	91.0(5)	N5–Cu1–N13	89.5(4)
N25–Cu2–N29	90.5(4)	N5–Cu1–N17	150.9(4)
N1–Cu1–N5	90.7(4)	N9–Cu1–N13	92.6(4)
N1–Cu1–N9	92.3(4)	N9–Cu1–N17	100.6(5)
N1–Cu1–N13	174.(4)	N13–Cu1–N17	87.7(5)
N1–Cu1–N17	89.6(5)		

semi-coordination position. So that the reason for the unusual geometry in this complex must be the 'lack' of space in this cationic layer, which avoids the presence of the six teec ligand for Cu(1) and making it possible for the polyoxometalate to act as a semi-coordinating ligand.

The other copper center, located in layer C, (Cu(2)) shows a distorted octahedral surrounding (see Fig. 3, right). The N–Cu–N angles vary between 87.5(5)° and 91.0(5)°. In these copper(II) centers, all three copper-ligand distances are quite different. This observation is in contrast to already published mononuclear six-coordinated copper(II) tetrazole compounds $[Cu(teec)_6](Anion)_2(teec)$ (with Anion is BF_4 or ClO_4) [18], where four of the teec ligands are at equal distance, and two ligands are positioned on the elongated *Jahn-Teller* axis. In the $[Cu(teec)_6]^{2+}$ center of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$, the three unique teec ligands are each at different distances (see Table 3). Because all ligands are the same, this difference in bond length must be caused by internal pressure, induced by the crystal packing.

Spectroscopic and magnetic properties

In the infrared spectrum of **1**, C–H stretching vibrations of the ligand are visible at 3136 cm^{-1} (CH tetrazole ring), 3024 and 2969 cm^{-1} (CH ethyl chain). Moreover, a characteristic signal of the polyoxometallate is visible at 1060 cm^{-1} (P–O).

Table 3. Selected bond lengths (Å) of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$

Atoms	Bond length (Å)
Cu2–N21	2.160(13)
Cu2–N25	2.040(11)
Cu2–N29	2.276(15)
Cu1–N1	2.001(11)
Cu1–N5	2.015(10)
Cu1–N9	2.224(11)
Cu1–N13	2.013(11)
Cu1–N17	2.035(11)

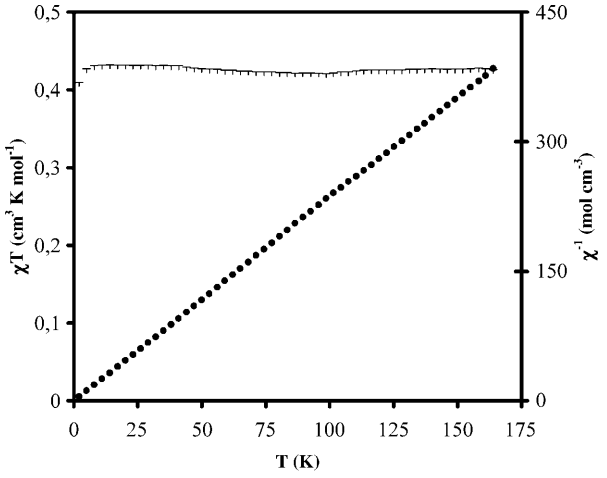

Fig. 5. Magnetic susceptibility of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$, with χT (+) and χ^{-1} (●)

In the EPR spectra of the solid at room temperature and at 77 K, only one anisotropic signal is seen with $g_\perp = 2.08$ and $g_{||} = 2.28$ ($g_{av} = 2.15$). The magnetic susceptibility has been determined in the temperature range 5–165 K. The plots of χ^{-1} versus the temperature and of χT versus the temperature (Fig. 5) show a *Curie* law, in full agreement with the structure which indicates that the Cu(II) ions are magnetically isolated. A *Curie* constant of $C = 0.425\,cm^3\,K\,mol^{-1}$ has been obtained. From this value one can calculate an average g parameter of 2.13 which is very close to that obtained from the EPR spectra.

Conclusions

The crystallization of teec with $Cu_3[PMo_{12}O_{40}]$ results in $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$, a layered structure containing both five- and six-surrounded copper(II) ions. This unusual set of Cu complexes in one compound is most likely caused by steric hindrance and crystal packing efficiency, induced by the large $[PMo_{12}O_{40}]^{3-}$ anions. To obtain a neutral complex, the ratio anion to cation must be 2 to 3. The lattice of the $[PMo_{12}O_{40}]^{3-}$ anions consists of layers at relatively equal distance, yielding alternating layers of distorted octahedrally surrounded $[Cu(teec)_6]^{2+}$ and distorted square-pyramidal surrounded $[Cu(teec)_5]^{2+}$ which also has an oxygen atom of the polyoxometalate semi-coordinated to this copper center.

Although the angles in $[Cu(teec)_6]^{2+}$ are close to octahedral, all three metal–ligand distances very considerably. In normal *Jahn–Teller* distorted octahedral CuL_6 systems, the four ligands positioned on the equatorial plane have all about the same metal–ligand distance, while the two axial ligands have a slightly longer bond length [19]. In $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$, the three axes of the $[Cu(teec)_6]^{2+}$ center are of different length (see Table 3).

In EPR, IR and ligand field spectroscopy no difference is observed between the five- and six-coordinated copper(II) anions, because the signals are superimposed.

The compound shows a *Curie* behavior, in agreement with the lack of interactions between the Cu(II) ions.

The complex can be considered as a good model system for the design of new compounds combining polyoxometalates and iron(II) spin-crossover cations, as the bulky polyoxoanions can impose an arrangement of the cations in isolated layers, so the elastic cooperativity may be studied in only two dimensions [30].

Experimental

Physical methods

Vis-NIR spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device (4000–300 cm^{-1}, res. 4 cm^{-1}). Magnetic susceptibility measurements (2–300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the *Pascal* constants [24]. C, H, N determinations were performed on a Perkin Elmer 2400 Series II analyzer. Microanalysis has been performed using an Environmental Scanning Electron Microscope (Philips, XL30 ESEM).

Synthesis

$Ag_3[PMo_{12}O_{40}]$

5.4 g of the *Keggin* acid $H_3[PMo_{12}O_{40}]$ (3.0 mmol) was dissolved in 40 ml of cold water. As soon as the solution was clear, a second solution of 1.7 g $AgNO_3$ (10.0 mmol) in approximately 5 ml of water has been added. A yellow precipitate formed immediately. The solution was stirred for another hour and then left at 4°C for 12 hours. The compound is obtained by filtration, washed with water and ether and dried on air. The yield consists of approximately 5.15 g (80%) of yellow powder.

From micro analysis, it has been concluded that all acidic protons are replaced by silver ions, and the molybdenum to silver ratio is 12:3. It has been concluded that the *Keggin* anion is still intact, as the phosphorous to molybdenum ratio is close to 1:12. In the infra-red spectrum, a characteristic signal is visible at 1059 cm^{-1}. Micro analysis (relative weight %): P 2.27, Mo 55.85, Ag 12.47%.

$Cu_3[PMo_{12}O_{40}]_2$

0.43 g of $Ag_3[PMo_{12}O_{40}]$ (0.2 mmol) were added in excess to a solution of 0.068 g of $CuCl_2 \cdot 2H_2O$ (0.4 mmol) in 7 ml of water. The poorly soluble *Keggin* salt reacts with the chloride ions, forming insoluble AgCl and very soluble $Cu_3[PMo_{12}O_{40}]_2$. This solution is, after filtration, added to a solution of 0.32 g teec (2.4 mmol) in 5 ml of alcohol. After one day, green, elongated plate-like crystals are formed.

Microanalysis confirms that both the polyoxometalate and copper are present. The copper to *Keggin* ratio is 3:2, whereas the copper to ligand ratio (determined by the amount of chloride) is 3:15, which is close to the expected 3:16. The ratio between the nitrogen and chloride confirms that no chloride ions, originating from copper(II) chloride, are present. Elemental analysis for $C_{48}H_{84}N_{64}Cu_3Cl_{16}P_2Mo_{24}O_{82}$, $\{[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O\}$; found (calc.): C 9.9 (9.6), H 1.5 (1.4), N 14.8 (15.0) %. Microanalysis: relative ratio found: N 17.23, Cu 1.67, P 1.74, Mo 12.83, Cl 8.33%.

Crystal structure determination and refinement

The crystal structure analysis was carried out on a green plate-like single crystal of $[Cu(teec)_5]_2[Cu(teec)_6][PMo_{12}O_{40}]_2 \cdot 2H_2O$ with approximate dimensions $0.48 \times 0.2 \times 0.05\,mm^3$. Relevant crystallographic data and structure determination parameters are given in Table 1. Selected angles and bond lengths are given in Tables 2 and 3, respectively. Cell parameters were obtained by the least-squares refinement method of 25 reflections. Intensity data were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation with the $\omega - 2\theta$ method. All calculations were carried out using the *WinGX* package [25]. The structure was solved by direct methods using the SIR 97 program [26], followed by *Fourier* synthesis, and refined of F^2 using the SHELXL-97 program [27]. *Lorentz*, polarization, and semiempirical absorption corrections (ψ-scan method) were applied to the intensity data.

One carbon atom of a teec ligand coordinated to Cu(1) (C(6A)) and a chloride atom of another teec ligand coordinated to Cu(2) (Cl(8A)) were found to be disordered over two positions with refined occupancies of 0.508/0.492 for C(6A)/C(6B) and 0.643/0.356 for Cl(8A)/Cl(8B). The occupancy factors of the two water molecules were refined, adopting values close to 0.5 and, in the next refinement they were fixed to these values and the O atoms were refined isotropically. All other non-H atoms were refined anisotropically. The positions of the hydrogen atoms were added in calculated positions and refined riding on the corresponding C atoms.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-196075 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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