Supplementary Information

A Direct Anchoring of Anderson-type Polyoxometalates in Aqueous Media with Tripodal Ligands Especially Containing Carboxyl Group

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Experimental Section

General methods and materials

All syntheses and manipulations were performed in the open air, all other chemicals, including solvents, were commercially available as reagent grade and used as received without further purification. $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ **(compound 3)** was synthesized according to literature methods[1]. IR spectra were measured using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. The mass spectra were obtained using an ion trap mass spectrometer (Thermofisher LTQ). Negative mode was chosen for the experiments (capillary voltage 33 V). Sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300 μL min^{-1}. Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). UV-Vis spectra were measured in acetonitrile with UV2100s spectrophotometer.

X-ray Crystallographic Structural Determinations

Suitable single crystals were selected. Data collections were performed at 100 K, by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, ver 2.30). Structures were solved by direct methods and refined against F^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. All calculations were carried out by the program package of SHELXTL Ver 5.1 [2] and Olex2 ver1.2[3].CCDC-963534, 963535, 963536 contains the supplementary crystallographic data for this compound **1-3** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

The synthesis of $[TBA]_3\{[CH_3C(CH_2O)_3]_2\,CrMo_6O_{18}\}$.2DMF, compound **1**:

3.213g $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and 0.72g $CH_3C(CH_2OH)_3$ were dissolve in 20ml H_2O then the solution was refluxing for at 100 °C for 3 h forming $[NH_4]_3\{[CH_3C(CH_2O)_3]_2\,CrMo_6O_{18}\}$,. Then it was precipitated from the aqueous by changing the equivalent amount of cation of TBA^+, the precipitation were redissolved in DMF. After recrystallization, the title compounds could be obtained as pink crystalline products (90% yields based on Mo). $C_{64}H_{140}N_5CrMo_6O_{26}$ m = 2023.47, H 6.95 C 37.97 N 3.48 while calcd H 6.97 C 37.99 N 3.46. IR (KBr pellet, major absorbances, cm^{-1}): 2961, 2874, 1480, 1384, 1050, 935, 914, 895, 794, 659. UV-Vis (MeCN, nm): λ_{LMCT} = 225, $\lambda_{d\text{-}d}$ =520. ESI mass spectrometry (MeCN): calcd m/z = 1634.79 $(TBA)_2\{[CH_3C(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 1393.32 $[H^+](TBA)\{[CH_3C(CH_2O)_3]_2\,CrMo_6O_{18}\}^-$, 1151.85 $[H^+]_2\{[CH_3C(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 696.16 $(TBA)\{[CH_3C(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$, 575.42 $[H^+]\{[CH_3C(CH_2O)_3]_2\,CrMo_6O_{18}\}^{2-}$, 383.28 $\{[CH_3C(CH_2O)_3]_2CrMo_6O_{18}\}^{3-}$; found 1634.78, 1393.54, 1151.78, 696.06, 575.66, 383.68, respectively.

The synthesis of $[TBA]_3\{[CH_3C(CH_2O)_2(COO)]_2\,CrMo_6O_{18}\}$.DMF, compound **2**:
The synthesis process and recrystallization is similar to synthesis of compound **1** while used equivalent amount of $CH_3C(CH_2OH)_2(COOH)$ instead of $(HOCH_2)_3CCH_3$ (90% yields based on Mo). $C_{61}H_{129}N_4CrMo_6O_{27}$ m = 1978.35, H 6.54 C 36.98 N 2.85 while calcd H 6.57 C 37.03 N 2.83. IR (KBr pellet, major absorbances, cm^{-1}): 2960 2935 2874 1715 1668 1480 1384 1218 1167 1105 1036 948 929 912 675. UV-Vis (MeCN, nm): λ_{LMCT} = 228, $\lambda_{d\text{-}d}$ =527.ESI mass spectrometry (MeCN): calcd m/z = 1662.78 $(TBA)_2\{[CH_3C(CH_2O)_2(COO)]_2CrMo_6O_{18}\}^-$, 1421.31 $[H^+](TBA)\{[CH_3C(CH_2O)_2(COO)]_2CrMo_6O_{18}\}^-$, 1179.84 $[H^+]_2\{[CH_3C(CH_2O)_2(COO)]_2CrMo_6O_{18}\}^-$, 710.15 $(TBA)\{[CH_3C(CH_2O)_2(COO)]_2\,CrMo_6O_{18}\}^{2-}$, 589.42 $[H^+]\{[CH_3C(CH_2O)_2(COO)]_2\,CrMo_6O_{18}\}^{2-}$, 392.61 $\{[CH_3C(CH_2O)_2(COO)]_2\,CrMo_6O_{18}\}^{3-}$; found 1662.58, 1421.64, 1179.76, 710.28, 589.64, 392.36, respectively.

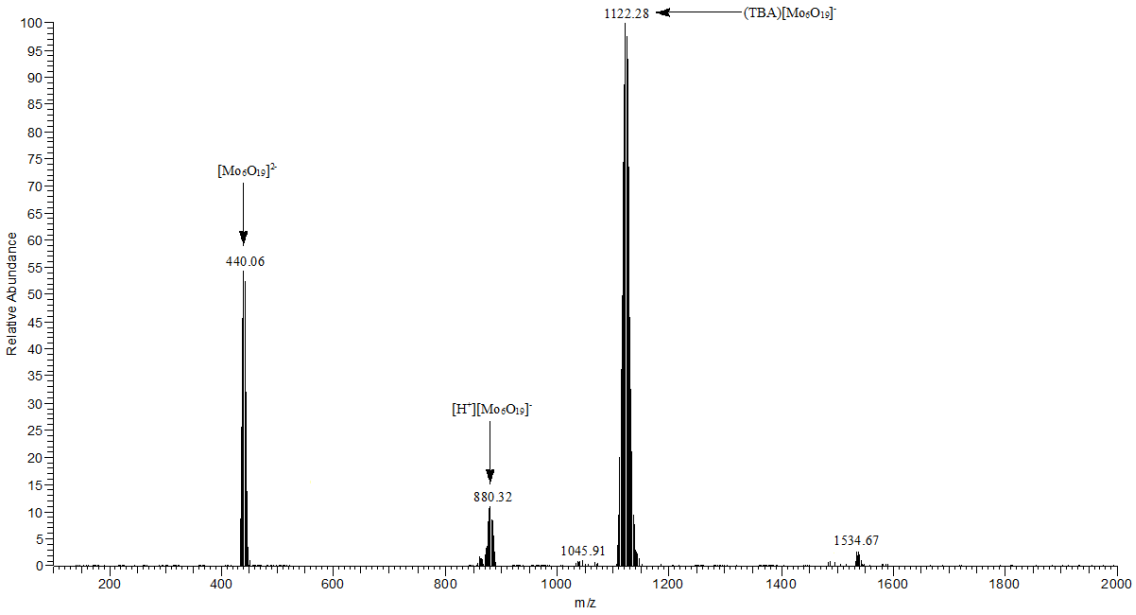
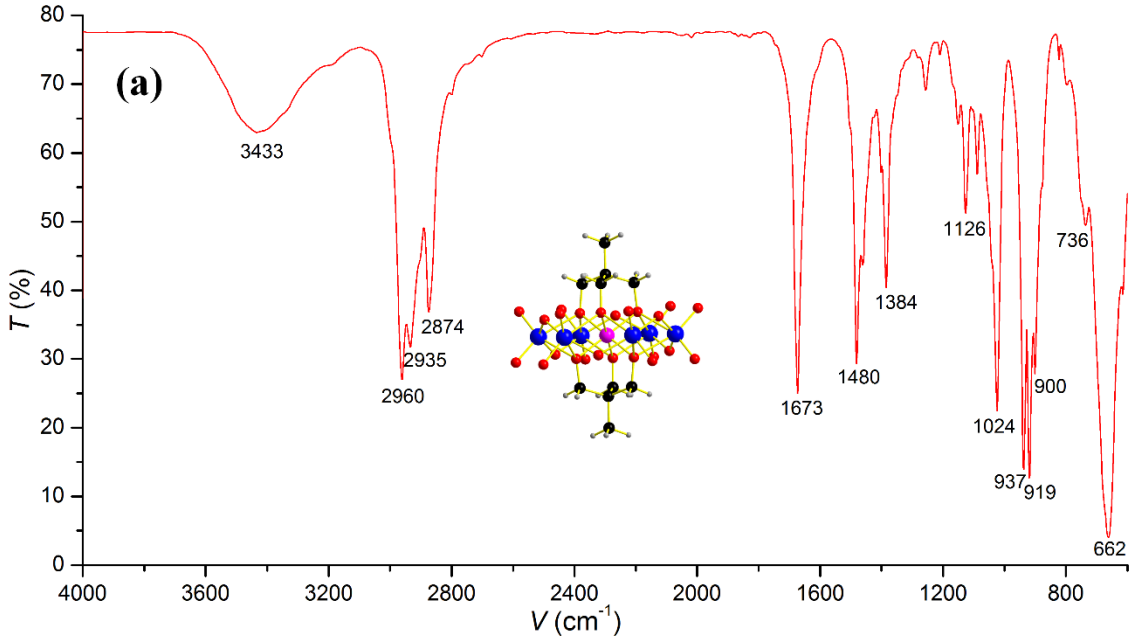


Figure S1. ESI mass spectra of substance obtained from $CH_3C(CH_2OH)_2(COOH)$ and $[TBA][Mo_8O_{26}]$ react in traditional one-pot protocol

ESI mass spectra of substance obtained from $CH_3C(CH_2OH)_2(COOH)$ and $[TBA][Mo_8O_{26}]$ react in traditional one-pot protocol which turn out to be the compound of $[TBA]_2[Mo_6O_{19}]$ (MeCN): $C_{32}H_{72}N_2Mo_6O_{19}$ m= 1364.57, calcd m/z=1122.11 $(TBA)[Mo_6O_{19}]^-$, 880.63 $[H^+][Mo_6O_{19}]^-$, 439.81 $[Mo_6O_{19}]^{2-}$, found 1122.28, 880.32, 440.06 respectively.



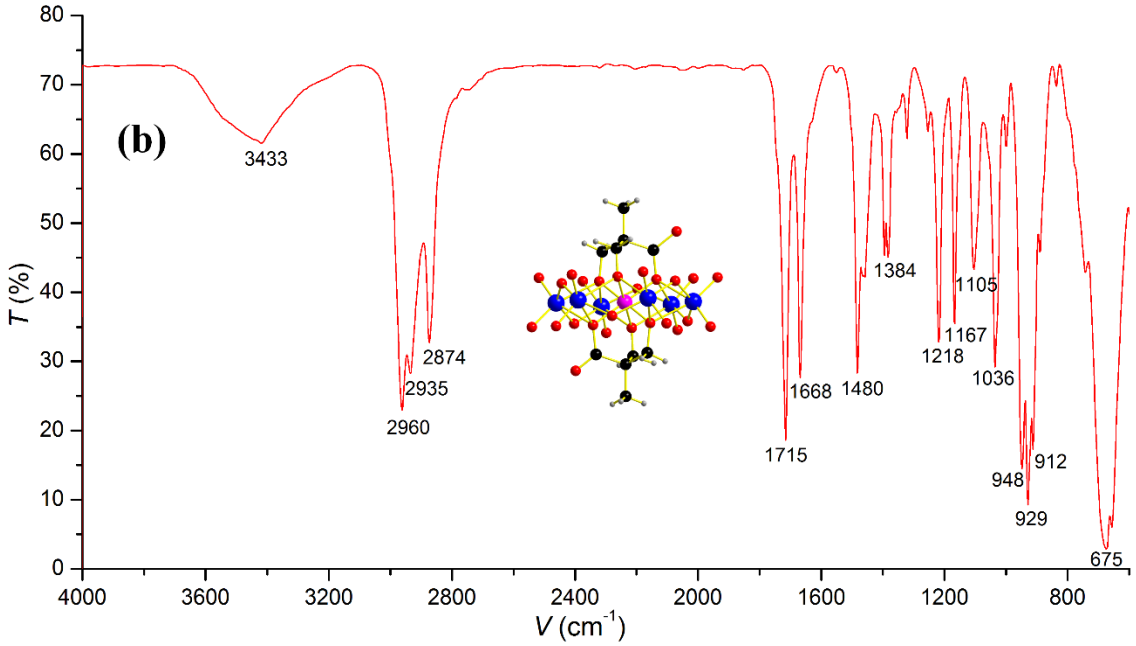
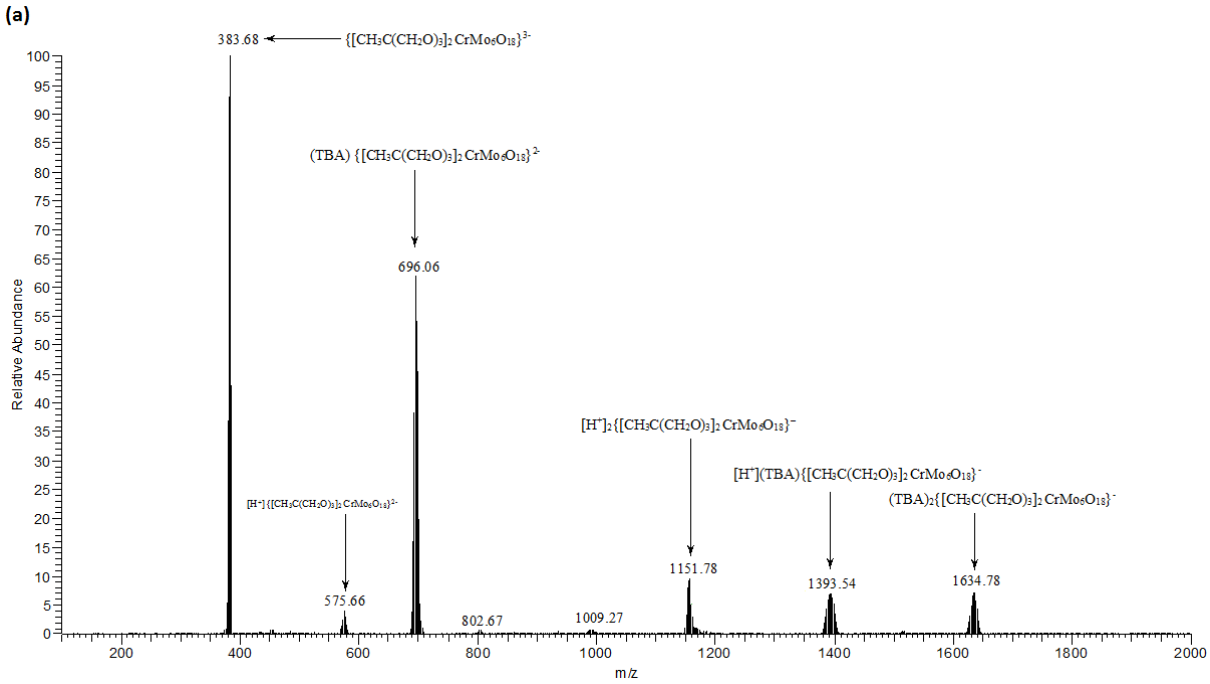


Figure S2. IR spectra of compound **1** (a) and compound **2** (b)



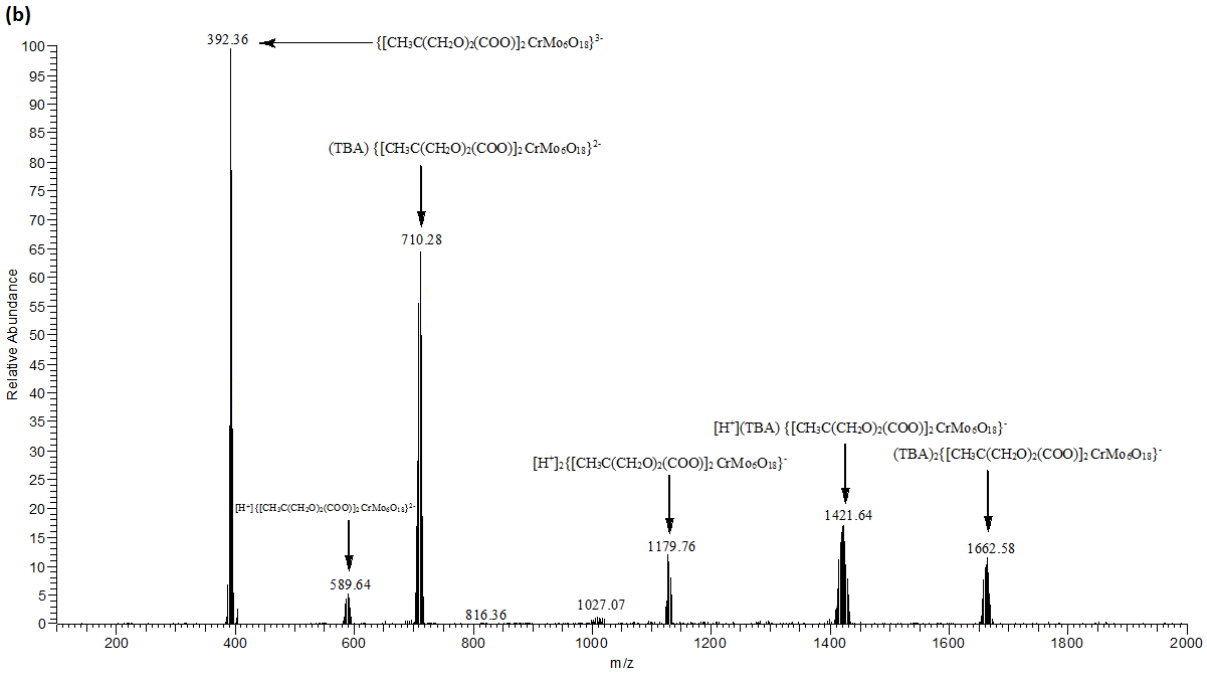
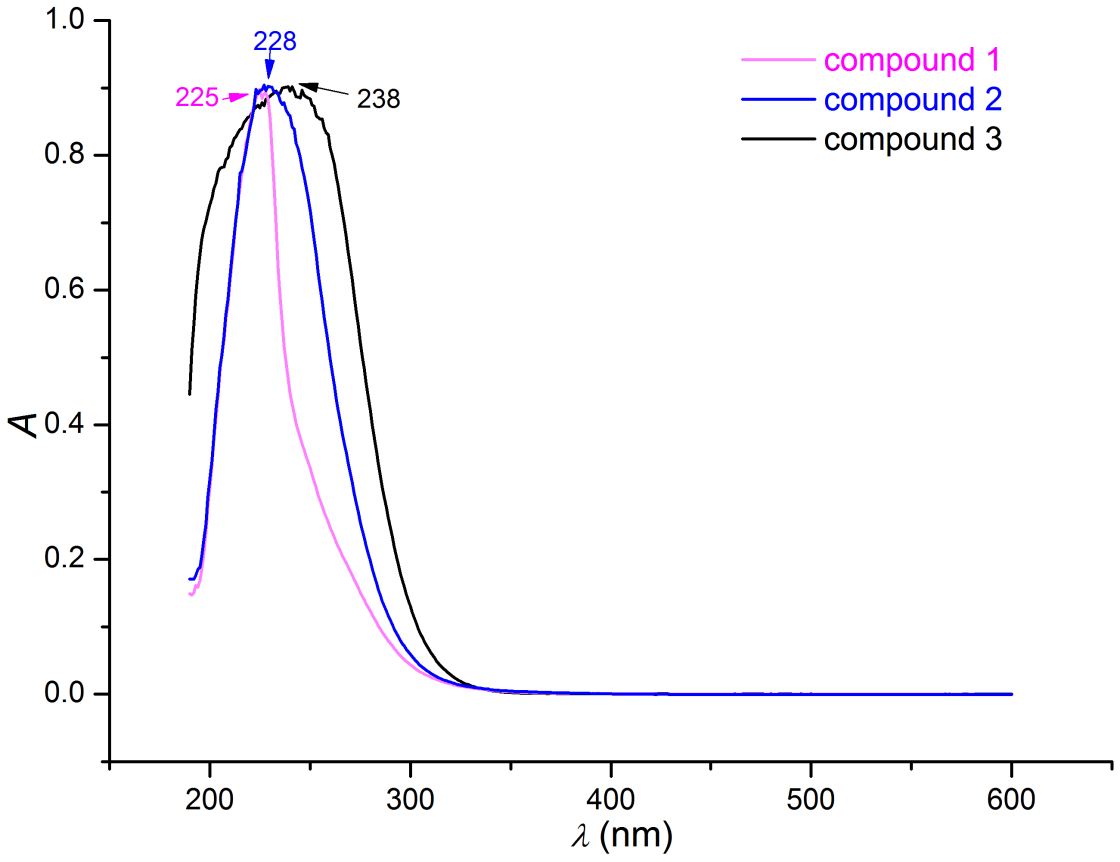


Figure S3. ESI mass spectra of compound **1** (a) and compound **2** (b)



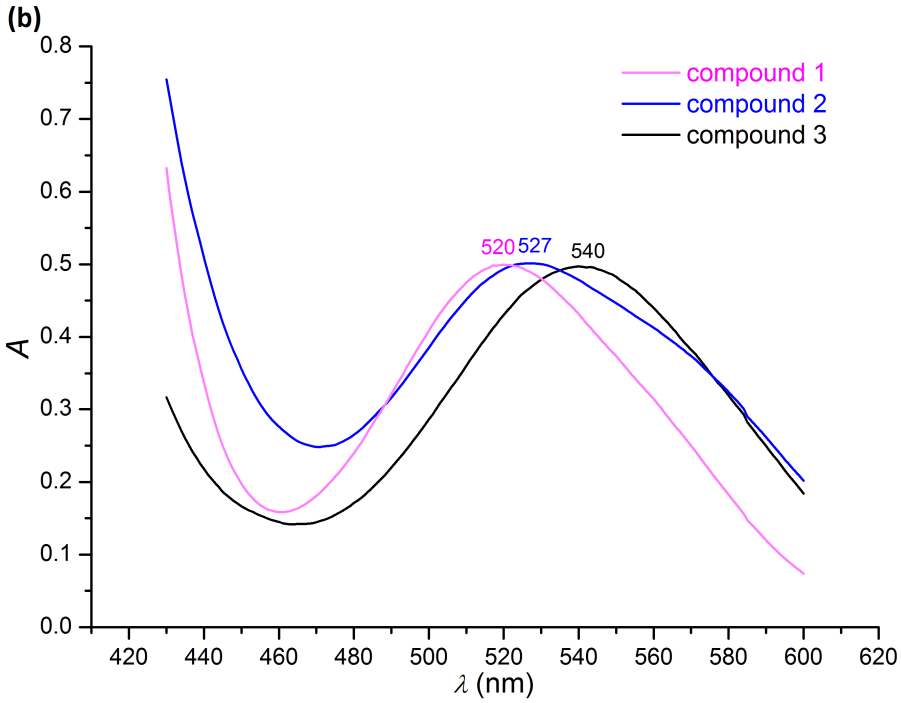
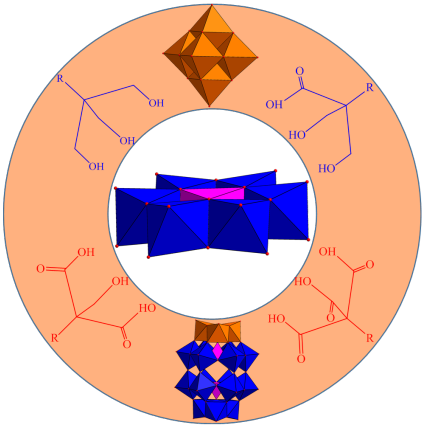


Figure S4. UV spectra of compound 1-3: LMCT (a) and d-d (b) transition.



Scheme 2. The design of functional tripodal ligands with carboxyl group and extension of Dawson, Lindquist type POMs.

Reference

[1] K. Nomiya, T. Takahashi, T. Shirai and M. Miwa, *Polyhedron*, 1987, **6**, 213-218.
[2]G. M. Sheldrick, *Acta. Crystallogr. A*, 2008, **64**, 112-122.
[3]O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.