The Chisholm–Cotton collaboration has provided a massive amount of data on molybdenum alkoxide structures,[25] mainly with bulky isopropoxy and *tert*-butoxy ligands. All would have electron counts grossly deficient from 18 if each alkoxide donated one electron. These compounds generally exhibit Mo–O bond lengths in the range 1.85–1.89 Å and Mo–O–C angles in the range 130–140°. As has been recognized by those authors,[26] Mo–O multiple bonding is indicated. Based on the ideas proposed here, the high reactivity of these dimers toward donor reagents may be as much related to alkoxide bending (creating an unsaturated metal center) as it is with the multiple metal–metal bond. Similarly, the isopropoxide ligand in $Mo(HBpz_3)(NO)Cl(O\text{-}i\text{-}Pr)$, where three-electron donation by alkoxide is required for an 18-electron configuration, forms a short Mo–O bond (1.863 Å) with a 132.4° angle at oxygen.[17]

In searching for soluble reagents which might effect some of the transformations shown by heterogeneous recipes,[2] the structural data reported here clearly indicates stronger Ti–O bonding, and therefore greater potential synthetic utility, in the monocyclopentadienyl species. As indicated above (eq 5), such compounds may be prepared by coupling (via carbon–carbon bond formation) of ketones using $[CpTiCl_2]_n$.[3] We will report subsequently on the transformation of these diolato dimers to deoxygenated organic products.

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Supplementary Material Available: A listing of anisotropic thermal parameters and observed and calculated structure factors for $Cp_2Ti(OC_2H_5)Cl$ and $[CpCl_2Ti]_2O_2C_2(CH_3)_4$ (38 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of Polypeptide Complexes of Dimolybdenum(II). 1. A Tetrakis(glycylglycine) Complex

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Abstract: The unique capacity of the Mo_2^{4+} cation to form complexes with polypeptide ligands in which only the carboxyl terminus is coordinated and the rest of the zwitterionic molecule is left conformationally free is described. This principle is then illustrated by the isolation and structural characterization of the $[Mo_2(\text{glycylglycine})_4]^{4+}$ ion in the form of the compound $[Mo_2(GG)_4]Cl_4\cdot6H_2O$. The structure has been solved and refined in space group $P\bar{1}$ with $Z = 1$ by conventional methods using diffractometer data. The unit cell dimensions are $a = 9.775$ (2) Å, $b = 10.886$ (2) Å, $c = 9.495$ (2) Å, $\alpha = 107.06$ (2)°, $\beta = 113.15$ (2)°, $\gamma = 91.07$ (2)°, $V = 877.8$ (1) Å^3. Each of the two crystallographically independent glycylglycine ligands contains a central peptide linkage that conforms very closely to the generally accepted standard dimensions and planar trans conformation for peptide links.

Introduction

Several years ago it was reported[1] that in aqueous solution the affinity of the carboxyl groups of amino acids for the Mo_2^{4+} ion, introduced conveniently as the chloro complex $[Mo_2Cl_8]^{4-}$, is very high, and one such compound, $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2\cdot3.5H_2O$, was isolated and structurally characterized. Recently the present authors have

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

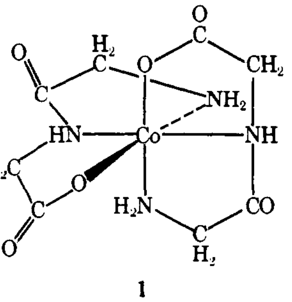
	x	y	z	$B(1.1)$	$B(2.2)$	$B(2.3)$	$B(1.2)$	$B(1.3)$	$B(2.3)$
Mo(1)	0.084 16(4)	0.067 73(3)	0.009 51(4)	1.62(1)	1.81(1)	1.40(1)	0.08(1)	0.536(9)	0.62(1)
Cl(1)	0.3478(1)	0.2211(1)	0.0415(2)	2.82(5)	3.73(5)	3.71(4)	0.20(4)	1.18(3)	1.80(4)
Cl(2)	0.8326(2)	0.3304(2)	0.3032(2)	4.06(6)	4.46(7)	3.72(5)	0.72(5)	1.45(4)	1.09(5)
O(1)	−0.0293(3)	0.0152(3)	0.2425(3)	2.4(1)	2.4(1)	1.7(1)	0.2(1)	0.99(8)	0.78(8)
O(2)	0.2475(3)	−0.0558(3)	0.0763(3)	1.8(1)	2.3(1)	2.3(1)	0.2(1)	0.77(8)	0.92(9)
O(3)	0.0660(3)	−0.1999(3)	0.0495(3)	2.1(1)	2.2(1)	2.3(1)	0.2(1)	0.84(8)	0.97(9)
O(4)	0.1418(3)	0.1622(3)	0.2582(3)	2.2(1)	2.4(1)	1.8(1)	0.1(1)	0.56(8)	0.60(9)
O(11)	0.2447(5)	−0.2943(4)	0.3680(4)	5.1(2)	3.4(2)	2.9(1)	−0.9(1)	1.5(1)	−0.0(1)
O(21)	0.3717(4)	0.0627(4)	0.5225(4)	3.2(1)	7.1(2)	5.1(1)	2.1(1)	2.77(9)	4.0(1)
Ow(1)	0.1610(7)	−0.6083(6)	−0.1562(7)	7.7(2)					
Ow(2)	0.4176(8)	−0.4943(7)	−0.1884(8)	8.9(2)					
Ow(3)	0.4230(8)	−0.6117(8)	0.5182(9)	10.3(2)					
N(11)	0.2577(5)	−0.3718(4)	0.1274(5)	3.4(2)	1.8(1)	2.5(1)	0.7(1)	1.3(1)	0.4(1)
N(12)	0.1367(7)	−0.5259(6)	0.3593(6)	9.2(3)	4.3(2)	5.2(2)	−2.2(2)	3.9(2)	0.2(2)
N(21)	0.1752(4)	0.0810(4)	0.5894(4)	2.4(1)	3.8(2)	1.8(1)	0.5(1)	1.1(1)	1.3(1)
N(24)	0.4639(5)	−0.1258(4)	0.6574(5)	2.8(2)	3.6(2)	2.7(2)	0.2(2)	0.4(1)	1.3(1)
C(11)	0.2032(5)	−0.1632(5)	0.0815(5)	2.3(2)	2.3(2)	1.3(1)	0.3(1)	0.5(1)	0.5(1)
C(12)	0.3184(5)	−0.2492(5)	0.1310(6)	2.4(2)	2.7(2)	2.6(2)	0.6(2)	0.9(1)	0.9(1)
C(13)	0.2224(6)	−0.3852(5)	0.2427(6)	2.5(2)	2.8(2)	2.3(2)	0.4(2)	0.5(1)	0.8(1)
C(14)	0.1548(6)	−0.5182(5)	0.2185(6)	3.9(2)	3.2(2)	2.8(2)	−0.1(2)	1.2(2)	0.7(2)
C(21)	0.0736(5)	0.1120(4)	0.3221(5)	2.6(2)	1.9(2)	1.8(1)	0.9(1)	1.0(1)	0.6(1)
C(22)	0.1180(6)	0.1720(5)	0.5029(5)	3.7(2)	3.3(2)	1.3(1)	0.8(2)	0.9(1)	0.4(1)
C(23)	0.3023(5)	0.0371(5)	0.5976(5)	2.5(2)	3.3(2)	1.9(2)	−0.1(2)	0.6(1)	0.8(1)
C(24)	0.3647(6)	−0.0419(5)	0.7093(6)	3.2(2)	3.9(2)	2.3(2)	0.8(2)	0.9(1)	1.3(2)
H(1)	0.127(5)	0.068(4)	0.635(5)	1.8(10)					
H(2)	0.251(4)	−0.421(4)	0.064(4)	0.6(8)					
H(3)	0.032(0)	0.199(0)	0.519(0)	5.0(0)					
H(4)	0.194(0)	0.245(0)	0.545(0)	5.0(0)					
H(5)	0.284(0)	−0.094(0)	0.706(0)	5.0(0)					
H(6)	0.420(0)	0.015(0)	0.817(0)	5.0(0)					
H(7)	0.503(0)	−0.175(0)	0.728(0)	5.0(0)					
H(8)	0.408(0)	−0.183(0)	0.550(0)	5.0(0)					
H(9)	0.545(0)	−0.073(0)	0.661(0)	5.0(0)					

	x	y	z	$B(1,1)$
H(10)	0.390(0)	−0.204(0)	0.238(0)	5.0(0)
H(11)	0.367(0)	−0.266(0)	0.059(0)	5.0(0)
H(12)	0.219(0)	−0.578(0)	0.196(0)	5.0(0)
H(13)	0.059(0)	−0.541(0)	0.129(0)	5.0(0)
H(14)	0.094(0)	−0.612(0)	0.339(0)	5.0(0)
H(15)	0.232(0)	−0.504(0)	−0.449(0)	5.0(0)
H(16)	0.072(0)	−0.467(0)	0.383(0)	5.0(0)

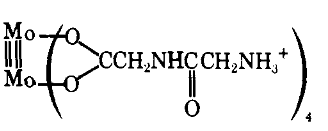
[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

looked more thoroughly into the consequences of this affinity and have reported several new amino acid compounds, all fully characterized as to structure. These include several other compounds containing the tetraglycine complex,[2] some mixed glycine and isoleucine thiocyanato complexes,[3] and a leucine complex.[4]

The ability of the Mo_2^{4+} ion to form complexes through attachment to the carboxyl groups of amino acids naturally led us to consideration of its use to form crystalline complexes of di- and polypeptides. Crystals obtained in this way were expected to be useful in the isolation of such peptides in forms suitable and convenient for structure analysis. The presence of the pair of heavy atoms can assist in the structure determinations without changing the inherent conformational preferences of the peptides. This is a situation unique to the Mo_2^{4+} unit as compared to all other metal ions that have been or might be employed to form complexes. In all other cases,[5,6] it would be expected, and is found, that the peptide binds to the metal ion through at least two of its potential donor sites and the conformation of the peptide is therefore seriously affected by the metal ion, to the extent that from the structure of the complex nothing can be learned as to the inherent structure of the uncomplexed peptide.



1



2

With particular regard to glycylglycine (HGG) complexes, we may illustrate the point just made with the structure of $Co(GG)_2$, shown schematically as **1**. It is seen that the terminal ammonium group has been deprotonated to give an anion, GG^-, and that two such anions serve as tridentate ligands. This may be contrasted with the way in which Mo_2^{4+} coordinates HGG, leaving it with a protonated terminal amino group and attaching itself only to the $-CO_2^-$ oxygen atoms, **2**.

Experimental Section

Preparation of $Mo_2(glycylglycine)_4Cl_4{\cdot}6H_2O$. $K_4Mo_2Cl_8$ (0.1 g), prepared by a literature method,[7] was dissolved in 50 mL of an aqueous solution (0.5 M) of glycylglycine and 0.5 M of HCl. The resulting yellow solution was kept under N_2 at ca. 25 °C. After 4 days yellow crystals were obtained.

X-ray Crystallography. A crystal of dimensions 0.15 × 0.10 × 0.15 mm was attached to the end of a glass fiber. Data were collected on a Syntex P$\bar{1}$ automated four-circle diffractometer using Mo Kα radiation (λ = 0.710 73 Å) with a graphite crystal monochromator in the incident beam. Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the triclinic system, with unit cell dimensions, obtained by a least-squares fit of 15 strong reflections in the range 25° < 2θ < 35°, of a = 9.775 (2) Å, b = 10.886 (2) Å, c = 9.495 (2) Å, α = 107.06 (2)°, β = 113.15 (2)°, γ = 91.07 (2)°, and V = 877.8 (1) Å^3.

Intensity data were measured by θ-2θ scans. A total of 2230 reflections in the range $0 < 2\theta \leq 50°$ were collected, of which 2044 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.[8] The data were corrected for Lorentz and polarization effects. The linear

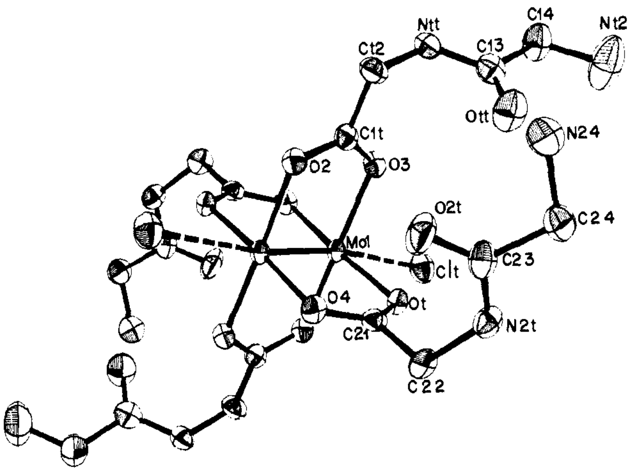


Figure 1. An ORTEP drawing of the centrosymmetric $[Mo_2(glycylglycine)_4]^{4+}$ ion and the two axially placed chloride ions. Thermal vibration ellipsoids are scaled to enclose 40% of the electron density.

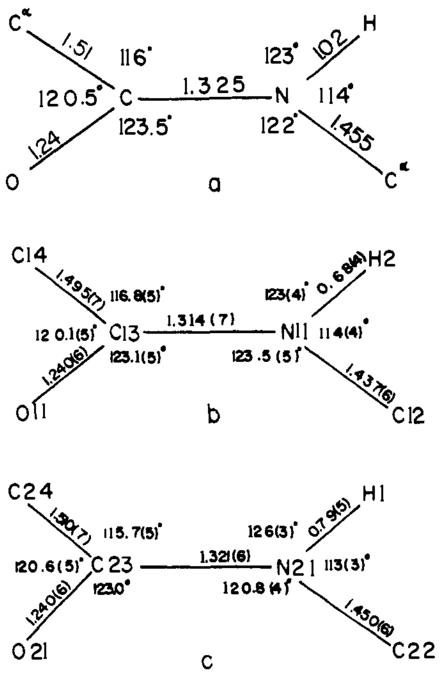


Figure 2. Dimensions of peptide units: (a) shows the "standard" dimensions;[10] (b) and (c) show the two crystallographically independent peptide units found in the $[Mo_2(GG)_4]^{4+}$ complex.

Table II. Bond Distances and Bond Angles for $Mo_2(gly\text{-}gly)_4Cl_4 \cdot 6H_2O$

	Bond Distances (Å)		
atoms	distance	atoms	distance
Mo(1)-Mo(1)′	2.106(1)		
-Cl(1)	2.907(1)		
-O(1)	2.129(3)		
-O(2)	2.132(3)		
-O(3)	2.108(3)		
-O(4)	2.111(3)		
O(1)-C(21)	1.260(5)	O(2)-C(11)	1.261(5)
O(4)-C(21)	1.270(5)	O(3)-C(11)	1.280(5)
C(21)-C(22)	1.520(6)	C(11)-C(12)	1.499(6)
C(22)-N(21)	1.450(6)	C(12)-N(11)	1.437(6)
N(21)-C(23)	1.321(6)	N(11)-C(13)	1.314(7)
C(23)-O(21)	1.240(6)	C(13)-O(11)	1.240(6)
-C(24)	1.510(7)	-C(14)	1.495(7)
C(24)-N(24)	1.471(7)	C(14)-N(12)	1.441(7)
N(21)-H(1)	0.79(5)	N(11)-H(2)	0.68(4)

	Bond Angles (deg)		
atoms	angle	atoms	angle
Mo(1)′-Mo(1)-Cl(1)	170.46(4)		
-O(1)	90.83(8)		
-O(2)	90.38(8)		
-O(3)	93.04(8)		
-O(4)	92.32(8)		
O(1)-Mo(1)-O(2)	93.6(1)		
-O(3)	87.7(1)		
-O(4)	176.2(1)		
O(2)-Mo(1)-O(3)	176.3(1)		
-O(4)	88.5(1)		
O(3)-Mo(1)-O(4)	90.0(1)		
Mo(1)-O(1)-C(21)	117.2(3)	Mo(1)-O(2)-C(11)	117.7(3)
Mo(1)-O(4)-C(21)	116.4(3)	Mo(1)-O(3)-C(11)	115.9(3)
O(1)-C(21)-O(4)	123.0(4)	O(2)-C(11)-O(3)	122.9(4)
-C(22)	118.7(4)	-C(12)	117.7(4)
O(4)-C(21)-C(22)	118.3(4)	O(3)-C(11)-C(12)	119.4(4)
C(21)-C(22)-N(21)	112.1(4)	C(11)-C(12)-N(11)	114.2(4)
C(22)-N(21)-C(23)	120.8(4)	C(12)-N(11)-C(13)	123.5(5)
N(21)-C(23)-O(21)	123.0(5)	N(11)-C(13)-O(11)	123.1(5)
-C(24)	115.7(5)	-C(14)	116.8(5)
O(21)-C(23)-C(24)	120.6(5)	O(11)-C(13)-C(14)	120.1(5)
C(23)-C(24)-N(24)	109.8(4)	C(13)-C(14)-N(12)	112.3(4)
C(22)-N(21)-H(1)	113(3)	C(12)-N(11)-H(2)	114(4)
C(23)-	126(3)	C(13)-	123(4)

absorption coefficient is 7.80 cm^{-1}; no absorption correction was applied.

The heavy-atom positions were obtained from a three-dimensional Patterson function, and the structure was refined[9] in space group $P\bar{1}$ to convergence using anisotropic thermal parameters for all the nonhydrogen atoms except the water oxygen atoms. Hydrogen atoms belonging to the water molecules were omitted but the 16 hydrogen atoms attached to the two HGG ligands were included. Only those two in the central peptide units, H(1) and H(2), were refined; the other seven on each ligand were introduced at calculated positions and assigned isotropic B values of 5.0.

The discrepancy indices, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, had final values of $R_1 = 0.037$, $R_2 = 0.056$ with an error in an observation of unit weight equal to 1.38. The final difference map showed no peaks of structural significance. A list of the observed and calculated structure factors is available as supplementary material.

Results and Discussion

The positional and thermal parameters of all atoms are listed in Table I. Figure 1 shows the structure of the $[Mo_2(GG)_4]^{4+}$ ion with the two chloride ions, Cl(1), that occupy axial positions. The other two chloride ions, Cl(2), are not in the vicinity of the metal atoms. The important interatomic distances and angles are listed in Table II.

The coordination stereochemistry of the Mo_2^{4+} ion is standard. The Mo-Mo distance, 2.106 (1) Å, is near the middle of the range for other such bonds in tetracarboxylato complexes,[1-4] and the mean Mo-O distance, 2.12 ± 0.01 Å, is also quite normal. The chloride ions along the Mo-Mo axis are very remote, 2.907 (1) Å, as is usual for axial ligands in $Mo_2(O_2CR)_4$ compounds. In short, as a dimolybdenum tetracarboxylate complex, this compound shows no unusual features.

The compound is interesting because it presents two almost chemically equivalent but crystallographically independent HGG units. The only small chemical difference between the two HGG units is in the pattern of hydrogen bonding to the carbonyl oxygen atoms and the terminal $-NH_3^+$ ions. N(24) is intramolecularly hydrogen bonded to O(11), whereas N(12) and O(21) form hydrogen bonds only to water molecules and/or adjacent molecules. All hydrogen bond distances are in the medium-to-long range (>2.7 Å) and show no features that require comment.

The two peptide units exemplify the dimensions charac-

Table III. Mean Planes for the Peptide Groups and Deviations Therefrom

plane 1: $0.2193X + 0.5854Y + 0.7805Z + 3.2632 = 0$
plane 2: $0.8106X - 0.3764Y + 0.4487Z + 3.8327 = 0$

Atoms Used to Defined Plane 1 and Their Deviations (Å), with esd's

C(24)	−0.054(5)	N(21)	0.047(4)
C(23)	0.021(5)	O(21)	0.007(4)
C(22)	−0.064(5)	H(1)	0.05(4)

Atoms Used to Define Plane 2 and Their Deviations (Å), with esd's

C(14)	0.015(6)	N(11)	−0.017(5)
C(13)	0.004(6)	O(11)	−0.005(5)
C(12)	0.019(6)	H(2)	−0.06(4)

teristic of a peptide linkage. As shown in Figure 2, the two independent sets of angles and distances agree well with each other and with the commonly accepted "standard" dimensions for a peptide unit.[10] The two peptide units examined here are also essentially planar as shown by the figures in Table III. No atom in the second one deviates from the mean plane by more than 3σ. In the first peptide unit there are larger deviations, three of which are as high as $10-12\sigma$. However, these are still quite small in absolute value (ca. 0.05 Å).

In summary, the complex we have studied appears to give, as expected, a convenient specimen (actually two independent ones) of the dipeptide unit, in a form that is unperturbed by coordination while retaining the considerable advantage of having two heavy atoms present to assist in the structure solution. We hope to extend this approach next to other di- and higher polypeptides, including those with chiral centers, in order to obtain accurate structural information on such peptides in a reasonably rapid and convenient way.

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Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of the Anionic Complex Potassium Dicyano(*meso*-tetraphenylporphinato)iron(III) Bis(acetone)

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Abstract: The synthesis and structural characterization of potassium dicyano(*meso*-tetraphenylporphinato)iron(III) bis(acetone) are reported. The material crystallizes with two formula units in space group $P2_1/n$ of the monoclinic system with cell dimensions of $a = 9.601$ (2) Å, $b = 11.439$ (2) Å, $c = 20.283$ (3) Å, and $\beta = 100.78$ (1)° at 20 °C. Measurement of diffracted intensities employed θ-2θ scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent data for $(\sin\theta)/\lambda < 0.67$ Å^{-1} were measured; 3873 reflections were retained as observed. These data were employed in the determination of structure and least-squares refinement. The final conventional and weighted discrepancy factors are 0.050 and 0.056, respectively. The [Fe(TPP)(CN)$_2$]$^-$ ion has crystallographically required C_i—$\bar{1}$ symmetry with an average Fe-N bond distance of 2.000 (6) Å. The Fe-C-N group is essentially linear with Fe-C = 1.975 (2) Å, in distinct contrast to the "bent" geometry found in cyano heme proteins.

Iron porphyrins serve as the prosthetic group for the biologically important class of proteins known as the hemoproteins. Our understanding of the variety of functions and reactions of the hemoproteins has been aided by ligand binding studies. These studies have been carried out on the hemoproteins[3] as well as model compounds, porphinatoiron complexes.[4] The strong binding of cyanide ion to ferric hemoproteins and porphinatoiron(III) species has been long recognized. Binding of the strong field cyano ligand leads to low-spin ferric derivatives and this feature has been utilized in a number of NMR studies of the hemoproteins[5,6] and porphinatoiron(III) derivatives.[7-11] Further, equilibrium studies have demonstrated[11,12] the stepwise binding of cyanide ion. These studies have been undertaken on dissolved species and surprisingly there are, to our knowledge, no published reports of the preparation of solid cyanoporphinatoiron(III) derivatives.[13] We report herein the preparation of the anionic complex dicyano-*meso*-tetraphenylporphinatoiron(III), [Fe(TPP)(CN)$_2$]$^-$, isolated as the K$^+$ salt, and its structural characterization.

Experimental Section

Synthesis of K[Fe(TPP)(CN)$_2$]·2(CH$_3$)$_2$C=O. [Fe(TPP)(H$_2$O)$_2$]-

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