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The Tetracyanopyrrolide Anion as Ligand in Transition Metal Complexes

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Abstract. Two isotypic mononuclear discrete complexes $[Co(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**1**) and $[Ni(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**2**) containing the tetracyanopyrrolide anion $[C_4(CN)_4N]^-$ (tcp) were synthesized from $[Me_4N]$tcp and the respective metal perchlorates in acetone/acetonitrile. Tcp coordinates to the transition metal atoms in η^1 fashion via the nitrogen atom of the pyrrole ring. No coordination via the cyano groups is observed. Both complexes show nearly ideal paramagnetic behavior according to the Curie law with magnetic moments of 4.98 μ_B for **1** and 3.09 μ_B for **2**. In the presence of Cu^{2+} ions tcp reacts with traces of water under hydrolysis of one cyano group to tricyanopyrrole-2-carboxamide $(NC_4(CN)_3C(O)NH_2)^-$ (tcpc). From solutions in DMF the complex $[Cu(tcpc)_2(DMF)_2]$ (**3**) is isolated.

Introduction

Cyanocarbons are a class of compounds that consist solely of C and N, known as neutral species and as anions. The functionality is mainly dominated by the large number of present cyano groups, which are strongly electron withdrawing and participate by resonance with the π system of the underlying carbon ring or chain. Cyanocarbon molecules are highly electron deficient and the respective anions weakly basic and weakly coordinating.[1] Azole ring based polynitriles [2] and cyano-substituted pyrroles [3] have been in the focus of theoretical investigations, showing the aromaticity, the stability versus oxidation and decreasing basicity with increasing number of CN groups. The pentacyanocyclopentadienide anion $[C_5(CN)_5]^-$ is a prominent member due to its high symmetry. The coordination chemistry of $[C_5(CN)_5]^-$ has received substantial attention during the last years for the preparation of metal-organic coordination polymers.[4–7] In contrast, the chemistry of its congener, in which a nitrogen atom replaces one ring carbon atom, namely the tetracyanopyrrolide anion (tcp) (Scheme 2) is still scarcely explored. Although the tcp anion was prepared already in 1980 by *Webster* et al. only one report about its structural chemistry has been published. H(tcp), Me(tcp), Me_4N(tcp), Na(tcp)•2.33THF, and EMIM(tcp) (EMIM = 1-ethyl-3-methylimidazolium) have been characterized by single-crystal X-ray diffraction.[9] This cyanocarbon ion attracted our attention because it has the potential for metal coordination, maintaining a classical σ coordination behavior either through CN groups, as has been found in the structure of Na(tcp)[9] or via the nitrogen atom of the pyrrole ring. Substitution of all hydrogen atoms of the underlying pyrrolide $C_4H_4N^-$ anion with four electron-withdrawing CN groups leads to dispersion the negative charge towards the peripheral cyano groups. Tcp may thus behave as a multifunctional ligand that gains particular interest in constructing metal-organic systems.

Results and Discussion

Synthesis and Properties

Tetramethylammonium tetracyanopyrrolide $[Me_4N]$tcp was synthesized according to the method reported by *Schulz* et al. and used as starting material in all attempts of preparation of transition metal complexes. The synthetic method employed for the formation of the complexes **1** and **2** is the metathesis reaction of $[Me_4N]$tcp with the perchlorates of Co^{2+} and Ni^{2+} as summarized in Scheme 1.

$$M(ClO_4)_2 + 2\,[Me_4N]tcp \xrightarrow{\text{acetone}} M(tcp)_2 + 2\,[Me_4N]ClO_4$$

$$M(tcp)_2 \xrightarrow{\text{MeCN}} [M(NCMe)_4(tcp)_2] \cdot 2\,MeCN$$

$$M = Co^{2+}, Ni^{2+}$$

Scheme 1. The synthetic route for the formation of complexes **1** and **2**.

Our experiments show that the coordination ability of tcp is rather weak. It turned out as essential to use a weakly coordinating anion with the used transition metal salts as essential for a successful synthesis (Scheme 2).

Water-free metal perchlorates $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in dry acetone as solvent were therefore used. On combining the metal perchlorates with $[Me_4N]$tcp, $[Me_4N]ClO_4$ precipitated out of the reaction mixture leaving only M^{2+} (M = Ni, Co) and the tcp anions in the solution. On recrystallization of the residues from acetonitrile the complexes $[Co(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**1**) and $[Ni(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**2**) were formed,

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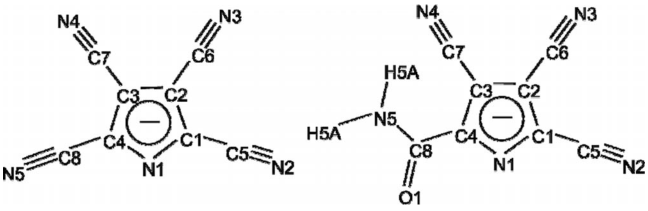

Scheme 2. Structural formulae and atom numbering scheme for (left) tetracyanopyrrolide (tcp) and (right) 3,4,5-tricyanopyrrole-2-carboxamide (tcpc) anions.

characterized by elemental and thermal analyses and magnetic measurements.

The thermal decomposition of the air stable complex **2** occurs in two stages in the temperature range 25–420 °C. The first mass loss of 12.6 % occurs between 90–130 °C with a DTA peak at 110.3 °C and is assigned to the release of the two solvate acetonitrile molecules (calculated weight loss 12.9 %). The second mass loss of 22.0 %, occurring between 140–190 °C (DTA peak at 176.1 °C) is attributed to the release of four coordinated MeCN molecules (calculated mass loss 25.8 %), leading to Ni(tcp)$_2$. The crystals of **1** have a pronounced tendency to lose the incorporated solvate molecules. Just on exposure to air, freshly prepared orange crystals of **1** become opaque after some minutes (Figure S3, Supporting Infomation). This limited stability of samples of **1** in air caused results of low accuracy with the thermal and elemental analyses in comparison to the nickel complex **2**. Thermal decomposition occurs in two stages with the first mass loss of 16.4 % beginning as low as 25 °C (DTA peak at 73.1 °C). The second detected mass loss of approx. 17 % can be contributed to the formation of Co(tcp)$_2$.

If water is not strictly excluded, the tetracyanopyrrolide anion can undergo hydrolysis under transformation of one cyano substituent to a carboxamide group, transforming tcp into tricyanopyrrole-2-carboxamide (tcpc). It is observed that this reaction occurs in the presence of Cu^{2+} ions and converts tcp within 3 d at room temperature completely. From DMF solutions, the copper(II) complex [Cu{NC$_4$(CN)$_3$C(O)NH$_2$}$_2$(DMF)$_2$] (**3**) could be isolated, which incorporates the mononegative tricyanopyrrole-2-carboxamide as a chelating ligand. This copper(II)-assisted hydrolysis to the corresponding amide under mild conditions is well known.[10,11] Complex **3** was characterized by X-ray diffraction only, since it was obtained as a by-product in small amounts.

Crystal Structures

Crystallographic data and details of structure determinations of compounds **1**, **2**, and **3** are shown in Table 1. The crystal structures of **1** and **2** are isotypic. Both contain mononuclear complexes with the central metal ions Co^{2+} and Ni^{2+} located in inversion centers. The metal atoms are each sixfold coordinated in a slightly distorted octahedral shape by two *trans*-positioned tcp ligands and four molecules of acetonitrile in the equatorial plane (Figure 1). The two axially bound tcp ligands are coordinated by their nitrogen atoms of the pyrrole rings in η^1 fashion. A sandwich structure with η^5-pyrrolide ligands as characteristic for bis(η^5-pyrrolide)cobalt or bis(η^5-pyrrolide)nickel[12,13] is not present, which is obviously caused by the low electron density in the central C$_4$N ring due to the strong electron-withdrawing effect of the nitrile substituents. The average angle *M*–N–centroid(tcp ring) equals 178°, indi-

Table 1. Crystallographic data and details of the structure refinements of compounds **1**–**3**.

	1	**2**	**3**
Formula	$C_{24}H_{12}N_{14}Co{\cdot}2(C_2H_3N)$	$C_{24}H_{12}N_{14}Ni{\cdot}2(C_2H_3N)$	$C_{22}H_{18}CuN_{12}O_4$
M_r /g·mol^{-1}	637.51	637.29	578.02
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	7.8693(2)	7.8384 (1)	6.4860(3)
b /Å	9.9411(3)	9.9108 (1)	9.9804(5)
c /Å	10.4822(3)	10.4508 (1)	10.5548(6)
α /°	96.171(2)	96.075 (1)	109.265(2)
β /°	102.334(2)	102.170 (1)	94.697(4)
γ /°	90.110(1)	89.896 (1)	101.619(4)
V /Å^3	796.19(4)	788.99 (2)	623.58(6)
D_{calc} /mg·m^{-3}	1.330	1.341	1.539
Z	1	1	1
μ /mm^{-1}	0.59	0.66	0.93
Crystal size /mm	0.13 × 0.10 × 0.10	0.16 × 0.11 × 0.09	0.16 × 0.07 × 0.04
Absorption correction	analytical	analytical	analytical
Range of data collection /°	$3.0 < \theta < 27.6°$	$3.0 < \theta < 30.1°$	$3.0 < \theta < 27.6°$
No. measured refl.	27031	29462	8797
No. independent refl.	3664	4614	2672
Data averaging R_{int}	0.071	0.039	0.075
Refined parameters	208	208	180
R ($F^2 > 2\sigma(F^2)$)	0.037	0.030	0.044
R (F^2) all refl.	0.055	0.037	0.067
wR (F^2)	0.077	0.073	0.097
Goodness of fit, S	1.06	1.05	1.04
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ /e·Å^{-3}	0.27 / –0.52	0.34 / –0.59	0.46 / –0.72

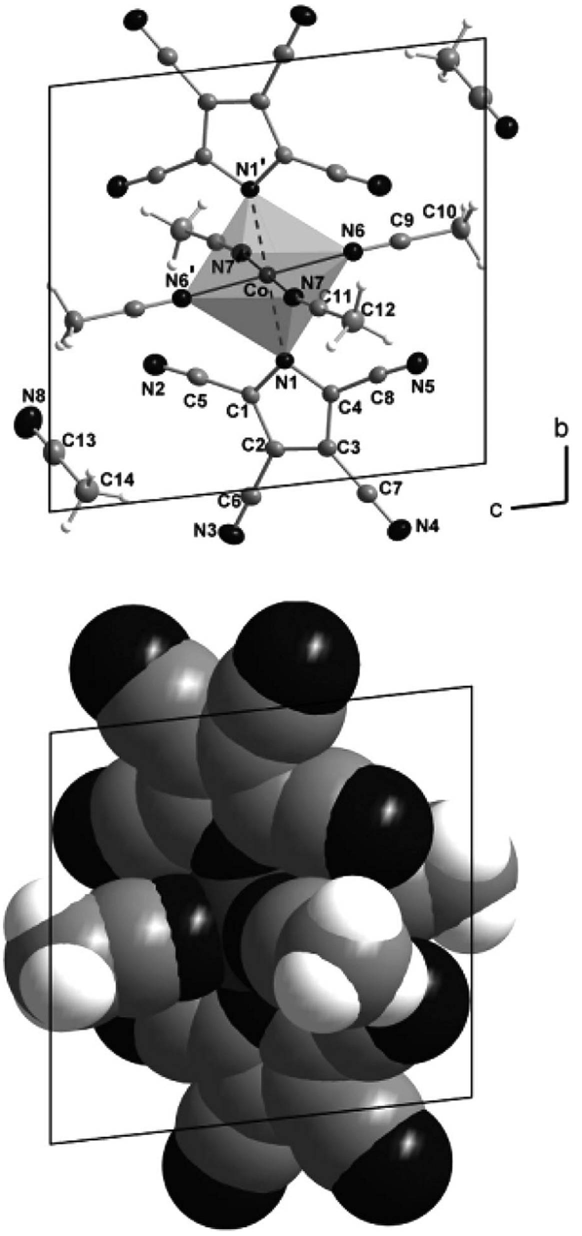

Figure 1. The crystal structure of $[Co(MeCN)_4(tcp)_2]{\cdot}2$ MeCN (**1**) in a view of the unit cell along the *a* axis. Displacement ellipsoids are drawn to enclose a 50 % probability. On bottom a space filling model of the complex is given to depict the high steric demand of the tcp ligand. The solvate CH_3CN molecules are omitted for clarity. Symmetry code: I = –*x*+1, –*y*+1, –*z*+1.

cating that the metal atoms are essentially in the plane of the C_4N ring, which is expected for a σ bonding situation. The bonds *M*–N(pyrrole) amount to 2.15 Å for **1** and 2.11 Å for **2** and are shorter than previously observed in Na(tcp) but slightly longer than those of the bonds *M*–NCMe in the equatorial planes (average *M*–N 2.12 Å for **1** and 2.07 Å for **2**). The tcp ligands are almost planar, the maximal deviation from the least square planes through all 13 atoms amounts to 0.09 Å for **1** and **2**. The C–N and C–C bond lengths within the pyrrole ring (1.362–1.409 Å), the exocyclic C–C bond lengths (1.423–1.436 Å) and the C≡N triple bond lengths (1.144–1.150 Å) reveal a good agreement with previously determined crystal structures involving this anion and the optimized structure obtained on basis of DFT calculations.[9] The tendency for delocalization of the π-electron system towards the peripheral cyano groups is displayed in the exocyclic C–C bond lengths, which are only slightly longer than those within the aromatic ring. The two nitrile substituents in the positions 2 and 5 of the pyrrole ring cause a high steric demand of this molecule when bound in the η^1-N mode, which becomes apparent in the space filling representation of the molecular structure (Figure 1). Complexes **1** and **2** adopt a similar structural arrangement as found for the complex $[Co\{C_5(CN)_5\}_2(H_2O)_2(thf)_2]$ $[C_5(CN)_5)^-$ = pentacyanocyclopentadienide anion], where the Co^{II} atom is coordinated by the nitrogen atoms of nitrile groups of two *trans* positioned $C_5(CN)_5$ ligands.[5] In the crystal of **1** and **2**, the shortest distance between the centroids of each two closest neighbored tcp ligands amounts to 4.36 Å, which excludes any π-stacking interactions.

In the crystal structure of $[Cu\{NC_4(CN)_3C(O)\text{-}NH_2\}_2(DMF)_2]$ (**3**), the central copper(II) atom is located in an inversion center and adopts an octahedral coordination (Figure 2). The equatorial positions are occupied by two symmetry related tcpc ligands, forming five-membered chelate rings in one plane, coordinating the central metal atom by the oxygen atom of the amide group and the nitrogen atom of the pyrrole ring. Two *trans*-positioned dimethylformamide molecules coordinate via their oxygen atoms almost perpendicular to this plane and complete the coordination arrangement around the central copper atoms to an elongated octahedron. A pronounced Jahn-Teller effect is present, manifested in largely differing bond lengths Cu–N(equat) = Cu–O(equat) = 1.99 Å and Cu–O(axial) = 2.55 Å. The tcpc ligand is essentially planar, the largest deviation from the plane through all 16 atoms amounts to 0.13 Å.

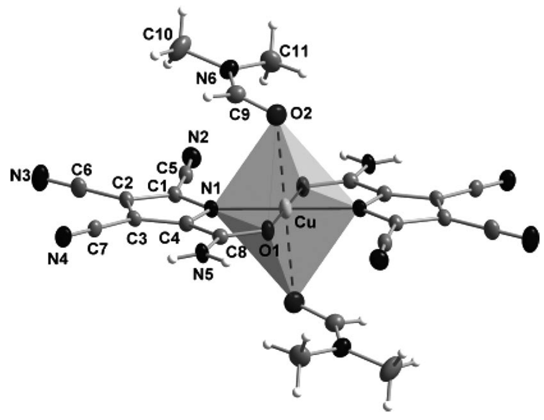

Figure 2. Structure of the discrete complex $[Cu\{NC_4(CN)_3C(O)NH_2\}_2(DMF)_2]$ (**3**). Displacement ellipsoids are drawn to enclose a 50 % probability, hydrogen atoms are drawn as small spheres.

Magnetic Properties

Magnetic susceptibility data of $[Ni(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**2**) and, due to its sensitivity $[Co(MeCN)_4(tcp)_2]{\cdot}2MeCN$ (**1**) with some loss of incorporated MeCN were recorded in the range of 1.9–300 K. Both complexes show nearly ideal Curie behavior in the full temperature range and therefore display regular paramagnetism. From the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{mol}}T)^{1/2}$ the calculated effective magnetic moment per Ni^{2+} ion in complex **2** at 300 K is 3.09 μ_B, which fits well with the free Ni^{2+} ion spin-only value for a $S = 1$ system ($\mu_{\mathrm{eff}} = 2.83\ \mu_B$) (see Supporting Information). According to the linear regression of the $\chi^{-1} = f(T)$ function for the cobalt(II) complex **1** (Figure 3) the susceptibility is consistent with a high spin complex of a magnetically isolated Co^{2+} ion in octahedral coordination. The experimental moment μ_{eff} at 300 K equals to 4.98 μ_B, which is substantially higher than the spin only value of $\mu_{\mathrm{eff}} = 3.87\ \mu_B$ calculated for a $S = 3/2$ system. The enlarged effective magnetic moment is typical for Co^{2+} and is explained by the contribution of the orbital angular momentum to magnetic moment.[14] The large M···M separation between the discrete complexes in the crystals excludes any significant metal–metal magnetic interactions and pure paramagnetism is present.

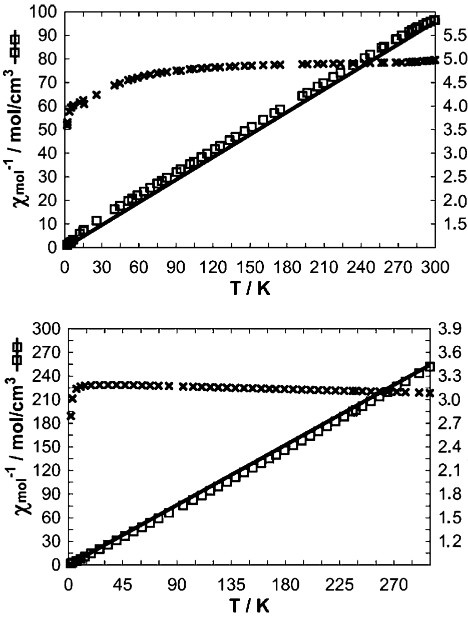

Figure 3. Plots of inverse susceptibility $\chi^{-1}(T)$ and the effective magnetic moments μ_{eff} as function of temperature for the high spin cobalt(II) complex **1** (top) and nickel(II) complex **2** (bottom). The experimental data correspond to open squares and cross points. The solid line represents the best fit to the Curie–Weiss model $\chi_{\mathrm{mol}} = C/(T - \Theta)$ with $\Theta = 0\ K$ for **1** and **2**.

Conclusions

The complexes $[\mathrm{Co(MeCN)_4(tcp)_2}]\cdot 2\mathrm{MeCN}$ (**1**) and $[\mathrm{Ni(MeCN)_4(tcp)_2}]\cdot 2\mathrm{MeCN}$ (**2**) show that the tetracyanopyrrolide anion acts as a monodentate ligand towards transition metal ions. Only the η^1-*N*-σ coordination mode via the lone electron pair of the nitrogen atom of the pyrrole ring was found. The other possible coordination modes, by the nitrogen atoms of the nitrile substituents as present in the structure of Na(tcp)[9] or the η^5-π coordination mode, have not been observed so far. Both complexes behave as diluted $S = 3/2$ ($\mathrm{Co^{II}}$, **1**) and S = 1 ($\mathrm{Ni^{II}}$, **2**) spin systems and obey the Curie law. In the presence of Cu^{2+} ions and even small amounts of water, tcp undergoes rapid hydrolysis under transformation of the cyano substituent in vicinal position to the ring nitrogen atom to a carboxamide group. The hydrolysis product tricyanopyrrolide-2-carboxamide tcpc acts as a bidentate ligand as found in the complex $[\mathrm{Cu(tcpc)_2(DMF)_2}]$ (**3**).

Experimental Section

Safety Note: Sodium cyanide is highly poisonous and liberates volatile HCN when mixed with acids. Organic perchlorates like $[\mathrm{Me_4N}]\mathrm{ClO_4}$ have to be treated as potential explosives and must therefore be handled with precautions; only small amounts should be prepared.

$\mathrm{Co(ClO_4)_2\cdot 6H_2O}$ and $\mathrm{Ni(ClO_4)_2\cdot 6H_2O}$ were dried under reduced pressure at 50 °C for about 5 h. Acetonitrile and acetone were stirred overnight with dry $\mathrm{K_2CO_3}$ and then distilled.

Tetramethylammonium Tetracyanopyrrolide $[\mathrm{Me_4N}]$tcp: The procedure mainly follows that given in Ref. [8] and with some modifications in Ref. [9]. Details are given in the Supporting Information.

Synthesis of $[\mathrm{Co(MeCN)_4(tcp)_2}]\cdot 2$ MeCN (1): Dry $[\mathrm{Me_4N}]$tcp (60 mg, 0.25 mmol) was dissolved in dry acetone (10 mL) and mixed with a solution of $\mathrm{Co(ClO_4)_2}$ (33 mg, 12 mmol) in dry acetone (10 mL). $[\mathrm{Me_4N}]\mathrm{ClO_4}$ precipitated as a white solid, which was filtered and discarded. The filtrate was evaporated to dryness and the solid residue was dissolved in dry acetonitrile. Slow evaporation of the solution (within about 6 d) produced orange crystals, which rapidly lost included solvent when taken out of the solution (see Supporting Information). Yield: 20 mg (20 %). M.p. >420 °C under decomposition. $\mathrm{C_{24}H_{12}N_{14}Co}$ (555.39 g·mol^{-1}): C 46.17 (calcd. 51.90); H 2.22 (2.18); N 32.63 (35.31) %.

Synthesis of $[\mathrm{Ni(MeCN)_4(tcp)_2}]\cdot 2$ MeCN (2): The synthetic procedure follows that of **1**, but with the use of $\mathrm{Ni(ClO_4)_2}$. The product was obtained 33 % yield as air stable violet crystals. M.p. >420 °C under decomposition. $\mathrm{C_{28}H_{18}N_{16}Ni}$ (637.27 g·mol^{-1}): C 52.02 (calcd. 52.72); H 2.89 (2.84); N 34.98 (35.16) %.

Synthesis of $[\mathrm{Cu\{NC_4(CN)_3C(O)NH_2\}_2(DMF)_2}]$ (3): $\mathrm{Co(ClO_4)_2\cdot 6H_2O}$ (23 mg, 0.06 mmol) was dissolved in acetone (10 mL). 5 mL of a solution of $[\mathrm{Me_4N}]$tcp (30 mg, 0.12 mmol) in acetone were added. $[\mathrm{Me_4N}]\mathrm{ClO_4}$ precipitated as a white solid, which was filtered off and discarded. The filtrate was evaporated to dryness and dissolved in DMF (3 mL). After 4 d, blue crystals in the shape of blocks appeared.

Crystal Structure Determinations: The crystals were selected immersed in perfluorinated oil and transferred in this medium into the cold nitrogen stream of the crystal cooling device of the diffractometer. Data collections were performed at –150 °C (123 K) with a Bruker-Nonius kappa-CCD diffractometer equipped with graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by Direct Methods and refined using the SHELX97 program suite.[15] Analytical absorption corrections were applied to all data sets.[16] Hydrogen atoms were refined in idealized positions as riding on their attached carbon atoms with isotropic displacement factors fixed to the value 1.5 of the respective carbon atoms. Graphical representations were made using the program DIAMOND.[17]

DTA/TG Measurements: TG-DTA analyses were performed with a thermoanalyzer STA 429 (Netzsch) in an argon atmosphere in the temperature range 20–420 °C.

Magnetic Measurements: The magnetic susceptibility measurements were performed with a Quantum Design PPMS Vibrating Sample Magnetometer (VSM) in the temperature range 1.9 to 300 K under an applied magnetic field of 10 kOe. Samples of weights 8.8 mg for **1** and 11.6 mg for **2** were used.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-999746 for **1**, CCDC-999747 for **2**, and CCDC-999748 for **3** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Detailed description of the synthesis and NMR spectra of [Me$_4$N]tcp, TG/DTA diagrams for complexes **1** and **2**, bond lengths and angles for the crystal structures of **1**, **2**, and **3**.

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References

[1] O. W. Webster, *J. Polym. Sci. A* **2002**, *40*, 210–221.
[2] P. Johansson, H. Nilsson, P. Jabcobsson, M. Armand, *Phys. Chem. Chem. Phys.* **2004**, *6*, 895–899.
[3] Rimarčík, V. Lukeš, E. Klein, M. Griesser, A.-M. Kelterer, *Chem. Phys.* **2008**, *353*, 177–184.
[4] R. J. Less, M. McPartlin, J. M. Rawson, P. T. Wood, D. S. Wright, *Chem. Eur. J.* **2010**, *16*, 13723.
[5] R. J. Less, T. C. Wilson, M. McPartlin, P. T. Wood, D. S. Wright, *Chem. Commun.* **2011**, *47*, 10007.
[6] R. J. Less, B. Guan, N. M. Muresan, M. McPartlin, E. Reisner, T. C. Wilson, D. S. Wright, *Dalton Trans.* **2012**, *41*, 5919.
[7] R. J. Less, T. C. Wilson, B. Guan, M. McPartlin, A. Steiner, P. T. Wood, D. S. Wright, *Eur. J. Inorg. Chem.* **2013**, *7*, 1161.
[8] H. E. Simmons, R. D. Vest, S. A. Vladuchick, O. W. Webster, *J. Org. Chem.* **1980**, *45*, 5113.
[9] M. Becker, J. Harloff, T. Jantz, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2012**, *34*, 5658.
[10] X.-Y. Ma, Y. He, Y.-L. Hu, M. Lu, *Tetrahedron Lett.* **2012**, *53*, 449.
[11] J. K. Bjernemose, Ch. J. McKenzie, P. Raithby, S. J. Teat, *Dalton Trans.* **2003**, 2639.
[12] N. Kuhn, M. Köckerling, S. Stubenrauch, D. Bläser, R. Boese, *J. Chem. Soc., Chem. Commun.* **1991**, 1368.
[13] N. Kuhn, G. Henkel, J. Kreutzberg, S. Stubenrauch, *J. Organomet. Chem.* **1993**, *456*, 97.
[14] H. Lueken, *Magnetochemie*, Teubner Publishers, Stuttgart, Germany, **1999**.
[15] G. M. Sheldrick, *SHELX97* [includes SHELXS97, SHELXL97, Ciftab], Programs for Crystal Structure Analysis, Universität Göttingen, Germany, **1998**.
[16] N. W. Alcock, *Cryst. Computing* **1977**, 271.
[17] *DIAMOND*, Program for Crystal Structure Visualisation, Crystal Impact Corp., Bonn, Germany, **2005**.

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