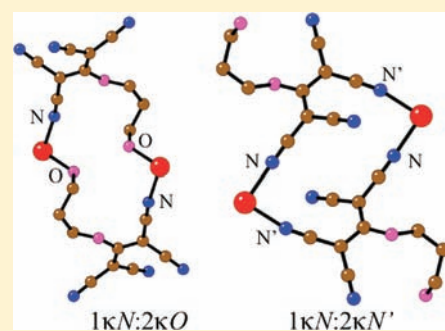


Linkage Isomerism in Coordination Polymers

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Supporting Information

ABSTRACT: The use of the recently prepared polynitrile ligand tcnopr3OH^- ($[(\text{NC})_2\text{CC}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH})\text{C}(\text{CN})_2]^-$) with different salts of Fe(II), Co(II), and Ni(II) has led to a very rare example of linkage isomerism in a coordination chain. These pairs of linkage isomers can be formulated as $[\text{M}(\text{tcnopr3OH}-\kappa\text{N},\kappa\text{O})_2(\text{H}_2\text{O})_2]$; M = Fe (1), Co (3), and Ni(5) and $[\text{M}(\text{tcnopr3OH}-\kappa\text{N},\kappa\text{N}')_2(\text{H}_2\text{O})_2]$; M = Fe (2), Co (4), and Ni (6). Compounds 1–2, 3–4, and 5–6 are three pairs of linkage isomers since they present the same formula and chain structure and they only differ in the connectivity of the polynitrile ligand bridging the metal ions in the chain: through a N and an O atom ($1\kappa\text{N}:2\kappa\text{O}$ -isomer) or through two N atoms ($1\kappa\text{N}:2\kappa\text{N}'$ -isomer). The magnetic properties show, as expected, very similar behaviors for both isomers.



INTRODUCTION

Linkage isomerism (LI) was first observed by Jørgensen¹ in 1894 and explained by Werner² in 1907 in the yellow ($\text{NO}_2-\kappa\text{N}$) and red ($\text{NO}_2-\kappa\text{O}$) isomers of the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$. Until the 1960s (when other metals and ligands as Rh^{III} , Ir^{III} , Pt^{IV} , Pd^{II} , Ni^{II} and SCN^- were found to present LI),^{3–6} the only known examples were Co^{III} complexes with the NO_2^- ligand in the *nitro* ($\text{nitrito}-\kappa\text{N}$) and *nitrito* ($\text{nitrito}-\kappa\text{O}$) coordination modes. In the late 1970s, Hauser et al. detected the formation of a low temperature metastable state (MS) in the nitroprusside salt $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]\cdot 2\text{H}_2\text{O}$ upon irradiation^{7,8} that was later characterized by Coppens et al. as a nitrosyl linkage metastable isomer.^{9–11} The possibility of using the phenomenon of LI as a bistability process to store information at the molecular level has raised an enormous interest in LI in the past decade, including new metals and ligands.^{12–23}

Depending on their stability, these complexes can be divided into two main groups: (1) those where both isomers are stable enough to be isolated and even crystallographically characterized and (2) those where one of the isomers is generated (usually at low temperatures) by an external stimulus as an induced metastable state (MS) generated by light irradiation at different wavelengths,^{9,11,12,24–33} pressure,³⁴ temperature,^{35–38} oxidation/reduction,^{39–46} or even protonation.^{36,37} Most of the few dozens of known couples of linkage isomers^{13,22,23,47–51} belong to the second group and, therefore, only one of the possible linkage isomers has been structurally characterized, except in some cases where photocystallography at low temperatures has allowed the structural characterization of the less stable isomer.^{9,29–33,52}

An exhaustive review of the literature shows that there are no more than 20 linkage isomers whose X-ray structure has been solved.^{53–77} From the structural point of view, most of the

known examples of LI are monomers^{9,29–33,52,55,56,60–66,69,71–73,75–77} although there are some dimers,^{53,54,57–59,67,68,74} a trimer,⁷⁰ and even a chain compound with Co(II) and chelidonate as ligand that has been very recently reported.⁷⁸ Therefore, the compounds presented in this work (see below) constitute very rare examples of LI in chain compounds and, as far as we know, the first case where the LI is observed in a chain with three different metal ions and the same ligand. The explanation for this very scarce number of known one-dimensional (1D) linkage isomers has several reasons: (i) the structural requirements of the bridging ligand which has to present at least three potentially coordinating sites with similar coordination capacity (or hardness in the HSAB terminology), (ii) the accessibility of these three coordinating sites has to be similar, (iii) the energy of both isomers also has to be similar, (iv) the kinetics of the transformation to the more stable isomer has to be slow enough, and (v) the size and charge density of the metal ion have to be adequate to fit in the different coordination spheres (see below).

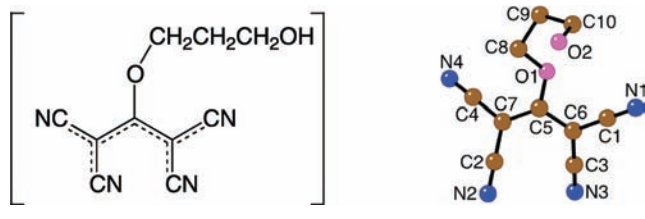
In the past decade, the use of polynitrile anions as coordinating ligands to construct polymeric architectures with interesting properties has been a burgeoning subject in Materials and Coordination Chemistry.^{79–84} This interest can be attributed to (i) the discovery of cyanide-bridged compounds of the Prussian blue (PB) family with long-range magnetic orderings even above room temperature⁸⁵ and (ii) the discovery of long-range magnetic ordering with huge coercive fields in some dicyanamide ($\text{dca}^- = [\text{NC}-\text{N}-\text{CN}]^-$) complexes with different transition metals.^{86–88} Polynitrile anions are versatile bricks that yield many different 0D, 1D, 2D, and 3D architectures with most 3d transition metals.^{89,90} This versatility

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is based in two main facts: (i) the ability to act as bridges, given the linear and rigid geometry of the cyano groups, and (ii) the possibility of functionalization with different potentially coordinating groups that leads to a high variety of coordination modes. To take advantage of both facts, we have recently prepared the polynitrile anion tcnopr3OH^- (= 1,1,3,3-tetracyano-2-(3-hydroxypropoxy)-propenide) which contains four $-\text{CN}$ groups and an additional potentially coordinating $-\text{prOH}$ group (Scheme 1).

Scheme 1. tcnopr3OH^- Polynitrile Ligand and Its Labeling Scheme in the Structures of This Work



The versatility of this ligand has been evidenced with the synthesis of an extensive series of polymeric complexes formulated as $[\text{M}(\text{tcnopr3OH})_2(\text{H}_2\text{O})_2]$ ($\text{M}^{\text{II}} = \text{Mn}, \text{Co}, \text{Ni}, \text{and Cu}$)⁹¹ whose structure consists of chains where each metal atom is connected to its neighbors through a double polynitrile bridge. Interestingly, in the Mn^{II} and Cu^{II} derivatives, the ligand coordinates the metal atoms through one $-\text{CN}$ group and the oxygen atom of the $-\text{prOH}$ group ($1\kappa\text{N}:2\kappa\text{O}$ -mode), whereas in the Co^{II} and Ni^{II} derivatives the polynitrile ligand coordinates the metals through two different $-\text{CN}$ groups ($1\kappa\text{N}:2\kappa\text{N}'$ -mode). This different behavior was attributed to the bigger size (in the Mn^{II} ion) and the bigger coordination flexibility (in the Cu^{II} ion), allowing the coordination of the $-\text{prOH}$ group, in contrast to the smaller Co^{II} and Ni^{II} ions. Since the size of Fe^{II} is in between that of Mn^{II} and Co^{II} , the Fe^{II} derivative might present either one or the other coordination modes (or even both modes). Accordingly, we have tried several synthetic routes using different precursor salts, temperatures and concentrations to prepare the Fe^{II} derivative in this series, and we have been able to isolate both coordination modes and, therefore, to prepare a couple of linkage isomers formulated as $[\text{Fe}(\text{tcnopr3OH}-1\kappa\text{N}:2\kappa\text{O})_2(\text{H}_2\text{O})_2]$ (1) and $[\text{Fe}(\text{tcnopr3OH}-1\kappa\text{N}:2\kappa\text{N}')_2(\text{H}_2\text{O})_2]$ (2). This result prompted us to perform a complete study to determine the exact conditions leading to one or other isomer and, even more, to determine if these synthetic conditions may also induce the same phenomenon in the other metal ions. This study has shown that Co^{II} and Ni^{II} also give rise to both linkage isomers: $[\text{M}(\text{tcnopr3OH}-$

$1\kappa\text{N}:2\kappa\text{O})_2(\text{H}_2\text{O})_2]$ $\text{M} = \text{Co}$ (3) and Ni (5) and the already known⁹¹ $[\text{M}(\text{tcnopr3OH}-1\kappa\text{N}:2\kappa\text{N}')_2(\text{H}_2\text{O})_2]$ $\text{M} = \text{Co}$ (4) and Ni (6) complexes.

RESULTS AND DISCUSSION

Synthesis. The six compounds were prepared by simple one-pot reactions of the ligand and metal solutions using different precursor salts (Table 1): $\text{Fe}(\text{ClO}_4)_2$, FeSO_4 , FeBr_2 , $\text{Fe}(\text{BF}_4)_2$, or $\text{Fe}(\text{CH}_3\text{COO})_2$ for 1; FeCl_2 for 2; $\text{Co}(\text{NO}_3)_2$, CoBr_2 , $\text{Co}(\text{BF}_4)_2$, or CoF_2 for 3; CoCl_2 , CoSO_4 , or $\text{Co}(\text{CH}_3\text{COO})_2$ for 4; $\text{Ni}(\text{BF}_4)_2$ or NiSO_4 for 5; and NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, or $\text{Ni}(\text{CH}_3\text{COO})_2$ for 6. Modification of the concentrations or the crystallization temperature did not produce any change in the final obtained phase. Although we have tried different conditions, the only factors influencing the final phase seem to be the counteranion and the metal ion. Thus, although the MCl_2 salts give the $1\kappa\text{N}:2\kappa\text{N}'$ isomers and the $\text{M}(\text{BF}_4)_2$ salts yield the $1\kappa\text{N}:2\kappa\text{O}$ isomers with the three metals ($\text{Fe}, \text{Co}, \text{and Ni}$), in contrast, the acetates yield different isomers depending on the metal ion ($1\kappa\text{N}:2\kappa\text{O}$ with Fe and $1\kappa\text{N}:2\kappa\text{N}'$ with Co and Ni). The sulfates also give different isomers depending on the metal ion ($1\kappa\text{N}:2\kappa\text{O}$ with Fe and Ni and $1\kappa\text{N}:2\kappa\text{N}'$ with Co). Although the list of precursors is far from being complete (Table 1), the data available to date suggests that the $1\kappa\text{N}:2\kappa\text{O}$ isomer might be more stable for Fe^{II} (five Fe^{II} salts produce the $1\kappa\text{N}:2\kappa\text{O}$ isomer but only one gives the $1\kappa\text{N}:2\kappa\text{N}'$ isomer) whereas for Co^{II} and Ni^{II} there is no clear preference for one or the other isomer (four Co^{II} and two Ni^{II} salts produce the $1\kappa\text{N}:2\kappa\text{O}$ isomer whereas three Co^{II} and three Ni^{II} salts give the $1\kappa\text{N}:2\kappa\text{N}'$ isomer). This observation suggests that the size of the metal atom might be an important factor determining the preference of one or the other isomer. Thus, the bigger ions Mn^{II} (ionic radius = 97 pm), Fe (92 pm), and Cu^{II} (87 pm) would mainly yield the $1\kappa\text{N}:2\kappa\text{O}$ isomer (Table 1) whereas, when the size of the ion decreases, the stability of the $1\kappa\text{N}:2\kappa\text{N}'$ would increase, becoming as stable as the $1\kappa\text{N}:2\kappa\text{O}$ isomer for Co^{II} (88.5 pm) and Ni^{II} (83 pm).⁹¹ Note that although Cu^{II} is slightly smaller than Co^{II} , the much higher coordination flexibility of Cu^{II} because of the presence of Jahn–Teller distortions confers on this element a much higher capacity to coordinate the $-\text{prOH}$ group of the ligand. To confirm this size-dependence of the obtained isomer, we have synthesized the Zn^{II} (88 pm) derivatives with different precursor salts (Table 1). To our surprise, the four prepared compounds present the $1\kappa\text{N}:2\kappa\text{O}$ isomer even though Zn^{II} has almost the same size than Co^{II} . Since the number of compounds prepared for each metal atom cannot be considered as statistically reliable, we have performed a complete search in

Table 1. Isomers Obtained with the 30 Different Precursor Salts and Metal Ions Used in This Work

M^{II}	$\sum(\text{M}-\text{O})^a$	$\sum(\text{M}-\text{N})^a$	$\text{O}-\text{N} (\%)^c$	F^-	Cl^-	Br^-	NO_3^-	BF_4^-	SO_4^{2-}	CH_3COO^-	ClO_4^-
Mn	22412	13186	70		N,O		N,O			N,O	N,O
Fe	15946	21362	-34		N,N'	N,O		N,O	N,O	N,O	N,O
Co	21208	26960	-27	N,O	N,N'	N,O	N,O	N,O	N,N'	N,N'	
Ni	20221	25937	-28		N,N' ^b		N,N'	N,O	N,O	N,N'	
Cu	15972	14778	8		N,O		N,O	N,O	N,O		
Zn	10466	8794	19		N,O		N,O	N,O	N,O		

^aTotal number of $\text{M}-\text{O}$ and $\text{M}-\text{N}$ bonds in hexacoordinated complexes of the type $\text{MO}_x\text{N}_{6-x}$ for each metal, after the CCDC database, (updated Nov. 2011). ^bThis $1\kappa\text{N}:2\kappa\text{N}'$ phase presents different unit cell parameters. The structural characterization shows that it is a $1\kappa\text{N}:2\kappa\text{N}'$ isomer although disorder in the $-\text{prOH}$ chain precludes a complete structural characterization. ^cDifference (in %) between the total number of $\text{M}-\text{O}$ bonds and $\text{M}-\text{N}$ bonds.

the CCDC database (updated Nov 2011) to try to understand the behavior of the different metal ions in hexacoordinated complexes with chromophores of the type $\text{MO}_x\text{N}_{6-x}$ ($x = 0-6$). This search shows that Mn^{II} , Cu^{II} , and Zn^{II} present a higher affinity toward O-donors than N-donors whereas Fe^{II} , Co^{II} , and Ni^{II} show the opposite tendency. Thus, in hexacoordinated complexes of the type $\text{MO}_x\text{N}_{6-x}$ the total number of M–O bonds exceeds that of M–N bonds (by 70%, 8%, and 19%, for Mn^{II} , Cu^{II} , and Zn^{II} , respectively, Table 1). Interestingly, these three metal ions only present the $1\kappa\text{N}:2\kappa\text{O}$ isomer. In contrast, for Fe^{II} , Co^{II} , and Ni^{II} , the total number of M–O bonds is lower than the number of M–N bonds (by 34%, 27% and 28% for Fe^{II} , Co^{II} , and Ni^{II} , respectively, Table 1). This preference for the N-donor ligands leads to the existence of the $1\kappa\text{N}:2\kappa\text{N}'$ isomer in these three metals. In summary, it seems that the $1\kappa\text{N}:2\kappa\text{O}$ isomer would be more stable in all cases (23 isomers $1\kappa\text{N}:2\kappa\text{O}$ vs 7 isomers $1\kappa\text{N}:2\kappa\text{N}'$, Table 1) and only those metals with higher affinity toward N-donors ligands (Fe^{II} , Co^{II} , and Ni^{II}) are able to form the $1\kappa\text{N}:2\kappa\text{N}'$ isomer (with a similar stability to that of the $1\kappa\text{N}:2\kappa\text{O}$ isomer). A tentative reason explaining the higher stability of the $1\kappa\text{N}:2\kappa\text{O}$ isomer would be the rigidity of the two $-\text{C}(\text{CN})_2$ wings of the ligand as compared to the much higher flexibility of the $-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ arm.

Nevertheless, at this point, we cannot explain what is the exact mechanism nor the counter-anions that, a priori, would lead to one or the other isomer. In any case, the intermediate size of the Fe^{II} , Co^{II} , and Ni^{II} ions and their higher affinity toward N-donors seems to be necessary to obtain the, probably less stable, $1\kappa\text{N}:2\kappa\text{N}'$ isomer.

Since both structural types have already been described, although for different metals,⁹¹ we will only focus on the differences observed for both isomers in the Fe^{II} , Co^{II} , and Ni^{II} derivatives. As can be seen in Figures 1 and 2, both linkage

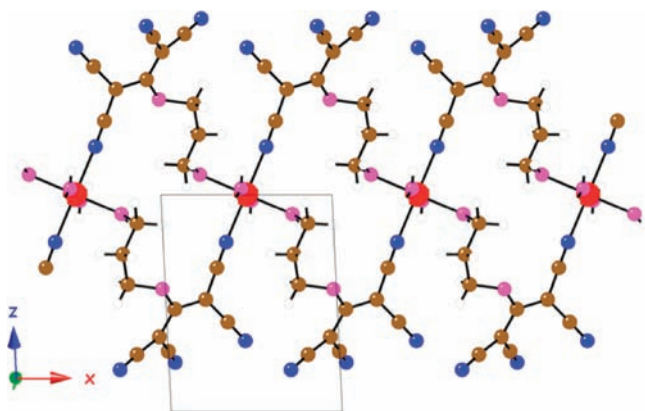


Figure 1. Chain structure of compound 1 showing the $1\kappa\text{N}:2\kappa\text{O}$ -coordination mode of the tcnopr3OH^- ligand. Color code: Fe = red, C = brown, H = white, O = pink, N = blue.

isomers present a chain structure where each M^{II} ion ($\text{M}^{\text{II}} = \text{Fe}^{\text{II}}$, Co^{II} , or Ni^{II}) is located on an inversion center and is connected by a double tcnopr3OH^- bridge with its two neighbors in the chain. Therefore, each M^{II} is connected to four tcnopr3OH^- ligands (acting as bis-monodentate) and two *trans* water molecules that complete the octahedral coordination of the M^{II} ions. The main difference between both compounds is the way in which the tcnopr3OH^- ligands bridge the M^{II} ions. In 1, 3, and 5 each ligand coordinates via a $-\text{CN}$ and the

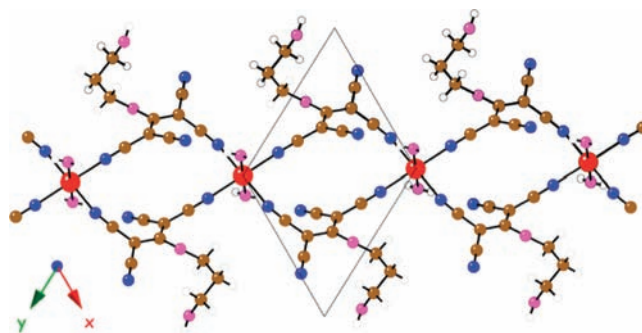


Figure 2. Chain structure of compound 2 showing the $1\kappa\text{N}:2\kappa\text{N}'$ -coordination mode of the tcnopr3OH^- ligand. Color code: Fe = red, C = brown, H = white, O = pink, N = blue.

terminal $-\text{OH}$ group ($1\kappa\text{N}:2\kappa\text{O}$ isomer, Figure 1) whereas in compounds 2, 4, and 6 the ligand uses two $-\text{CN}$ groups from two different $-\text{C}(\text{CN})_2$ wings ($1\kappa\text{N}:2\kappa\text{N}'$ isomer, Figure 2). Since the dimensionality of the derivatives remains unchanged and the formula is also the same, these different coordination modes originate, as far as we know, the first structurally characterized pairs of linkage isomeric chains with the same ligand and three different metal ions.

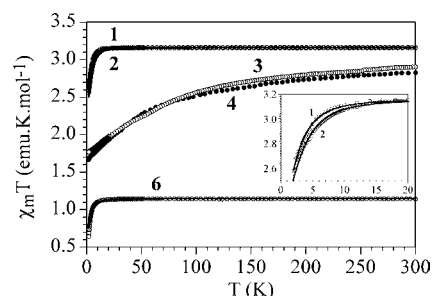
In the Fe^{II} derivatives (as well as in the other couples of isomers) the coordination environments of the metal ions are similar except for the already mentioned N/O LI, resulting in FeN_2O_4 and FeN_4O_2 environments in 1 and 2, respectively. The analysis of the bond distances and angles reveals that the $1\kappa\text{N}:2\kappa\text{O}$ coordination mode produces slight changes in the Fe coordination environment and in the ligand geometry. Thus, in 1 the $\text{Fe}-\text{O}_{2\text{prOH}}$ bond is 0.016 Å longer than the $\text{Fe}-\text{O}_{3\text{water}}$ one, suggesting the presence of a weak tension in the first bond, whereas the other two bonds ($\text{Fe}-\text{O}_{3\text{water}}$ and $\text{Fe}-\text{N1}$) are 0.013 Å and 0.006 Å longer in 1 than in 2 (see Supporting Information). On the other hand, the coordination of the $-\text{OH}$ group of the tcnopr3OH^- ligand in the $1\kappa\text{N}:2\kappa\text{O}$ isomer produces a straightening of the $-\text{prOH}$ arm, as evidenced by the $\text{C9}-\text{C10}-\text{O2}$ bond angle that increases from $109.2(2)^\circ$ in 2 to $112.4(3)^\circ$ in 1 (see Supporting Information) resulting in a longer $\text{C5}\cdots\text{O2}$ distance in 1 (4.51 Å vs 4.15 Å in 2). The rigidity of the central $(\text{NC})_2\text{CCC}(\text{CN})_2$ skeleton is evidenced by the fact that the *trans* disposition of the coordinated CN groups leads to a longer intrachain Fe–Fe distance in 2 (8.7239(7) Å) than in 1 (7.1199(6) Å) even if the number of atoms in the bridge is shorter ($-\text{NCCCCCN}-$ in 2, compared to $-\text{NCCCCOCH}_2\text{CH}_2\text{CH}_2\text{O}-$ in 1).

Both isomers present interchain interactions thanks to the presence of some interchains H-bonds. The main difference between both isomers is due to the presence of a terminal $-\text{prOH}$ group in the $1\kappa\text{N}:2\kappa\text{N}'$ isomer which is available to form H-bonds. Thus, the $1\kappa\text{N}:2\kappa\text{O}$ isomers (1, 3, and 5) present H-bonds formed only by the H atoms of the coordinated water molecules (O3) and the N atoms of the noncoordinated $-\text{CN}$ groups (N2 and N4, Table 2), leading to the 3D arrangement depicted in Figure 3a. In contrast, the $1\kappa\text{N}:2\kappa\text{N}'$ isomers (2, 4, and 6) present two types of H-bonds: (i) $\text{O}\cdots\text{H}-\text{O}$ between the H atoms of the water molecules (O3) and the terminal $-\text{OH}$ group (O2) and (ii) $\text{N}\cdots\text{H}-\text{O}$, between the terminal $-\text{OH}$ group (O2) and one non coordinated $-\text{CN}$ group (N4, Table 2). These two types of H-bonds lead to the 3D network shown in Figure 3b.

Table 2. Bond Distances (Å) and Angles (deg) of the Interchain H-Bonds Formed in Both Isomers

compound	H-bond	D...A	H...A	\angle D-H...A
1κN:2κO-Fe (1)	O3-H2...N4	2.83	2.04	175.0
	O2-H3...N2	2.77	2.01	174.7
1κN:2κN'-Fe (2)	O3-H2...O2	2.66	1.88	163.5
	O2-H3...N4	2.81	1.98	176.2
1κN:2κO-Co (3)	O3-H2...N4	2.82	2.06	176.8
	O2-H3...N2	2.78	2.04	174.6
1κN:2κN'-Co (4)	O3-H2...O2	2.67	1.91	156.5
	O2-H3...N4	2.80	1.76	175.8
1κN:2κN'-Ni (6)	O3-H2...O2	2.68	2.01	137.1
	O2-H3...N4	2.79	1.84	159.7

Magnetic Properties. In both Fe(II) derivatives (1 and 2) the room temperature $\chi_m T$ values are the same (3.15 emu K mol⁻¹, close to the expected value for a high spin, $S = 2$ Fe^{II} ion) and show a very similar thermal behavior: they remain constant when lowering the temperature down to about 10 K and show an abrupt decrease to reach a value of 2.60 emu K mol⁻¹ at 2 K (Figure 4). This behavior indicates that both compounds are essentially paramagnetic and present a zero field splitting (ZFS) of the $S = 2$ spin ground state. Accordingly, we have fit the magnetic data to a $S = 2$ monomer with a ZFS⁹² and obtained a very good agreement with the experimental data in the whole temperature range with $g = 2.053$ and $|D| = 2.0$ cm⁻¹ for 1 and $g = 2.053$ and $|D| = 2.4$ cm⁻¹ for 2 (solid lines in Figure 4). As expected, the two cobalt isomers (3 and 4) also present very similar magnetic behaviors (Figure 4) with a $\chi_m T$ value at room temperature of about 2.9 emu K mol⁻¹, in the normal range of the $\chi_m T$ values observed for high spin Co(II) octahedral complexes and higher than the expected value for a $S = 3/2$ spin ground state because of the orbital contribution arising from the ground ⁴T_{1g} term.⁹³ On lowering the temperature, the $\chi_m T$ product shows the typical continuous decrease because of the spin-orbit coupling. Finally, the only magnetically characterized Ni^{II} isomer (compound 6) shows a $\chi_m T$ value of about 1.15 emu K mol⁻¹ in the temperature range 300–20 K and a progressive decrease at lower temperatures. This behavior can be well reproduced by a simple model of an $S = 1$ monomer with a ZFS with $g = 2.139$ and $|D| = 3.7$ cm⁻¹ (solid line in Figure 4). Note that the value of the ZFS in all cases might include a very weak interchain antiferromagnetic interaction mediated by the H-bonds. The essentially paramagnetic behavior observed in the five compounds is not surprising since the tcnopr3OH⁻ ligand provides in both isomers a long pathway that is not able to promote an effective

**Figure 4.** Thermal variation of the $\chi_m T$ product for compounds 1–4 and 6. Inset shows the low temperature region of the Fe derivatives. Solid lines are the best fit to the model (see text).

magnetic coupling, as previously observed in the Mn and Cu derivatives with the same ligand.⁹¹

CONCLUSIONS

In summary, the use of the tcnopr3OH⁻ ligand, bearing up to five potentially coordinating groups, has led to the synthesis of the first couples of linkage isomers with a chain structure observed for three different metals. The presence of five different potentially coordination sites (four –CN and one –OH group) and the flexibility of the –prOH arm in the ligand has allowed the isolation and structural characterization of two linkage isomers: [M(tcnopr3OH-1κN:2κO)₂(H₂O)₂] and [M-(tcnopr3OH-1κN:2κN')₂(H₂O)₂] (M = Fe, Co, and Ni). These couples of linkage isomers represent three of the very scarce examples of LI where both isomers are stable enough to be isolated and structurally characterized and are, as far as we know, the first examples of linkage isomers in a chain compound with three different metals.

EXPERIMENTAL SECTION

Synthesis of [Fe(tcnopr3OH-1κN:2κO)₂(H₂O)₂] (1), [Fe-(tcnopr3OH-1κN:2κN')₂(H₂O)₂] (2), [Co(tcnopr3OH-1κN:2κO)₂(H₂O)₂] (3), [Co(tcnopr3OH-1κN:2κN')₂(H₂O)₂] (4), [Ni(tcnopr3OH-1κN:2κO)₂(H₂O)₂] (5), and [Ni(tcnopr3OH-1κN:2κN')₂(H₂O)₂] (6). Although all the isomers, except compound 2, can be prepared with different precursor salts, the procedures we describe here are those that yielded the best single crystals in each case. The six compounds were prepared by heating aqueous solutions (2 mL) of FeSO₄·7H₂O (140 mg, 0.5 mmol, for 1), FeCl₂·4H₂O (99 mg, 0.5 mmol for 2), Co(NO₃)₂·6H₂O (145.5 mg; 0.5 mmol for 3), CoCl₂·6H₂O (118.5 mg; 0.5 mmol for 4), Ni(BF₄)₂·6H₂O (170.2 mg; 0.5 mmol for 5), or Ni(NO₃)₂·4H₂O (124.4 mg; 0.5 mmol for 6) and Ktcnopr3OH (252 mg, 1 mmol, 5 mL)⁹¹ resulting in yellowish (for 1), whitish (for 2), orange (for 3 and 4), and pale green (for 5 and 6)

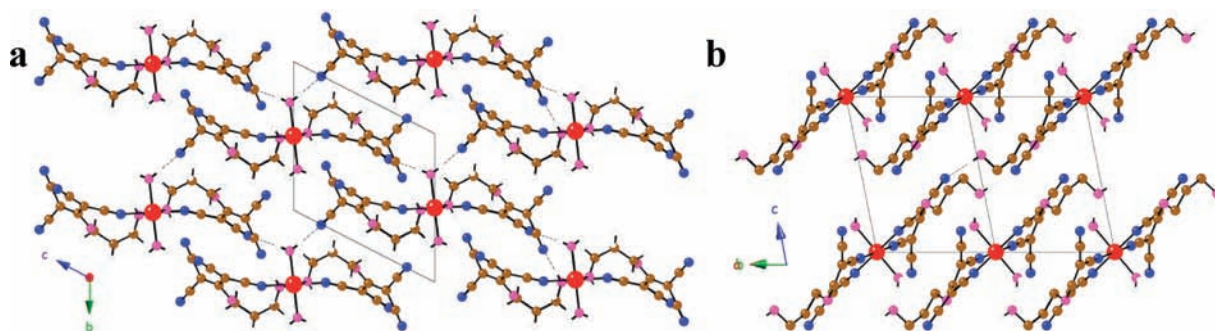
**Figure 3.** Interchain H-bonds in (a) the 1κN:2κO isomers (1, 3, and 5) and (b) the 1κN:2κN' isomers (2, 4, and 6). Color code: Fe = red, Co = brown, H = white, O = pink, N = blue.

Table 3. Crystal Data and Structural Refinement Parameters for Compounds $[M(\text{tcnopr}3\text{OH}-1\kappa\text{N}:2\kappa\text{O})_2(\text{H}_2\text{O})_2]$, $M = \text{Fe}$ (1), Co (3), and Ni (5), and $[M(\text{tcnopr}3\text{OH}-1\kappa\text{N}:2\kappa\text{N})_2(\text{H}_2\text{O})_2]$, $M = \text{Fe}$ (2), Co (4), and Ni (6)

empirical formula ^a	$\text{C}_{20}\text{H}_{18}\text{FeN}_8\text{O}_6$ (1)	$\text{C}_{20}\text{H}_{18}\text{FeN}_8\text{O}_6$ (2)	$\text{C}_{20}\text{H}_{18}\text{CoN}_8\text{O}_6$ (3)	$\text{C}_{20}\text{H}_{18}\text{CoN}_8\text{O}_6$ (4)	$\text{C}_{20}\text{H}_{18}\text{NiN}_8\text{O}_6$ (5)	$\text{C}_{20}\text{H}_{18}\text{NiN}_8\text{O}_6$ (6)
molecular weight	522.27	522.27	525.35	525.35	525.13	525.35
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	7.1015(3)	8.3149(4)	7.104(5)	8.241(5)	7.25(3)	8.199(5)
<i>b</i> (Å)	9.3503(4)	8.6723(5)	9.321(5)	8.600(5)	9.28(2)	8.556(5)
<i>c</i> (Å)	10.0191(4)	9.7332(4)	9.972(5)	9.702(5)	9.89(4)	9.687(5)
α (deg)	116.376(4)	84.645(4)	116.352(5)	84.701(5)	115.8(3)	85.008(5)
β (deg)	91.428(4)	76.533(4)	91.592(5)	76.369(5)	91.5(4)	76.128(5)
γ (deg)	91.882(4)	61.760(5)	92.152(5)	62.156(5)	92.7(3)	61.975(5)
<i>V</i> (Å ³)	595.12(4)	601.20(5)	590.5(6)	590.7(6)	598(4)	582.1(6)
<i>Z</i>	1	1	1	1	1	1
<i>T</i> (K)	170	170	120	120	298	120
ρ_{calc} (g cm ⁻³)	1.457	1.443	1.477	1.477		1.498
μ (cm ⁻¹)	6.86	6.79	7.79	7.79		8.87
<i>F</i> (000)	268	268	269	269		270
reflections measured	3920	3268	3325	4934		5147
2θ range (deg)	7.34–46.50	5.34–50.34	7.16–46.50	6.38–56.56		5.78–59.94
reflections unique/ <i>R</i> _{int}	1700/0.021	1474/0.016	1691/0.019	2849/0.0237		2919/0.103
reflections with <i>I</i> > 2 σ (<i>I</i>)	1650	1260	1645	2675		1997
<i>N</i> _v	196	196	196	196		193
<i>R</i> ₁ ^b / <i>wR</i> ₂ ^c	0.0210/0.0535	0.0254/0.0615	0.0218/0.0538	0.0321/0.0815		0.0661/0.1295
GoF ^d	1.064	1.060	1.064	1.055		0.926
$\Delta\rho_{\text{max, min}}$ (e Å ⁻³)	+0.195, -0.202	+0.223/-0.136	+0.182/-0.265	+0.471/-0.392		+1.028/-0.741

^aThe empirical formula corresponds to two asymmetric units. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^2] \}^{1/2}$. ^dGoF = $\{ \sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{var}}) \}^{1/2}$.

precipitates that were filtered off. Slow evaporation of the mother solutions at room temperature afforded colorless needles and plates (for 1 and 2, respectively), orange prisms (for 3 and 4), and very light green plates (for 5 and 6) single crystals suitable for X-ray structure determination. Elem. anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_6\text{Fe}$ (1 and 2): C, 46.00; H, 3.47; N, 21.46. Found: C, 44.88; H, 3.72; N, 21.04 (for 1) Found: C, 45.76; H, 3.46; N, 21.55 (for 2). Elem. anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_6\text{Co}$ (3 and 4): C, 45.73; H, 3.45; N, 21.33. Found: C, 44.95; H, 3.36; N, 21.36 (for 3) Found: C, 45.45; H, 3.42; N, 21.48 (for 4). Elem. anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_6\text{Ni}$ (5 and 6): C, 45.75; H, 3.45; N, 21.34. Found: C, 44.82; H, 3.45; N, 21.19 (for 5) Found: C, 45.45; H, 3.42; N, 21.60 (for 6).

Magnetic measurements were carried out in the temperature range 2–300 K with an applied magnetic field of 0.1 T on polycrystalline samples (with masses of 66.82, 22.13, 83.51, 35.93, and 51.39 mg for 1–4 and 6, respectively) with a Quantum Design MPMS-XL-5 SQUID magnetometer. The data were corrected for the sample holder and the diamagnetic contributions ($\chi_{\text{dia}} = -306.2 \times 10^{-6}$ for 1 and 2 and -305.2×10^{-6} emu.mol⁻¹ for 3, 4, and 6).

X-ray Structure Determination. Crystallographic data were collected at 120 K (170 for compounds 1 and 2) using an Oxford Diffraction Xcalibur 2 Diffractometer (monochromated MoK α radiation, $\lambda = 0.71073$ Å). The unit cell determinations and data reductions were performed using the CrysAlis program suite on the full set of data.⁹⁴ For all compounds, the crystal structures were solved by direct methods and successive Fourier difference syntheses with the Sir97 program⁹⁵ and refined on *F*² by weighted anisotropic full-matrix least-squares methods using the SHELXL97 program.⁹⁶ Both software were used within the WINGX package.⁹⁷ All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located by difference Fourier map, and then refined isotropically for all compounds. Scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography.⁹⁸ Data collection and refinement parameters are given in Table 3. Further details are provided in the Supporting Information.

■ ASSOCIATED CONTENT

● Supporting Information

Figures with the labeling scheme for both isomers and tables with selected bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre free of charge (CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) on quoting the depository numbers CCDC-848171, CCDC-675203, CCDC-848172, CCDC-848173, and CCDC-848174 for 1, 2, 3, 4, and 6, respectively.

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