

Cyanide-Promoted Demetalation of TrpyNiNCO: A Route to Sensitive Metallotripyrrens of Co^{II}, Fe^{II}, and Mn^{II}

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Etheral solutions of free base tripyrrens (HTpy) were prepared by treatment of nickel isocyanate complexes (TrpyNiNCO) with excess cyanide. From these solutions sensitive metallotripyrrens with cobalt(II), iron(II), and manganese(II) ions (TrpyMX) and with a choice of external ligands X could be obtained in pure, crystalline form. Four cobalt and one iron chelate were characterized by X-ray crystallography. Tetracoordinate cobalt(II) species with X = I, NCO, and NCS displayed unstrained tetrahedral coordination geometries, whereas the pentacoordinate TrpyCoNO₃ with the O,O-nitrato ligand narrows a trigonal bipyramidal coordination. TrpyFeNCO undergoes a redox-transformation to (TrpyFeNCO)₂O upon crystallization and was structurally characterized as this with an almost linear Fe–O–Fe subunit. Donor association was studied by UV–vis spectroscopy employing different solvents and showed that TrpyMnX and TrpyFeX species are very prone to the formation of pentacoordinate species, whereas TrpyCoX compounds have an intermediate tendency to do so. Nevertheless, complex fragments of all three metal ions form 1D coordination polymers with dicyanamido ligands, which were investigated by means of IR and SQUID measurements.

Introduction

The continued interest in the coordination properties of nonnatural porphyrinoids has lately resulted in a number of reports dealing with metal chelates of N,N,N-bound oligopyrrolic macrocycles like N-confused porphyrins,¹ p-benziporphyrins,² texaphyrins,³ and others⁴ (Figure 1). Within

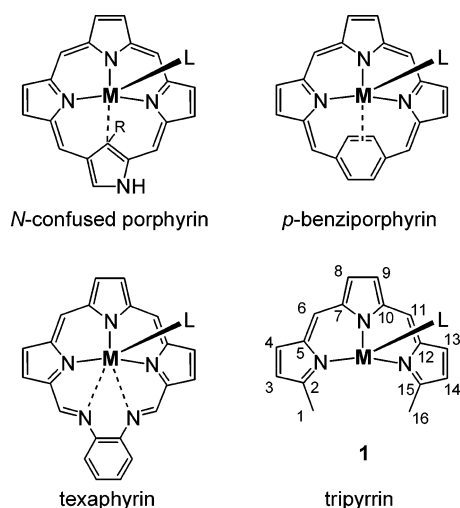


Figure 1. N,N,N-Binding mode in macrocyclic porphyrinoids and in tripyrren 1.

this group of macrocycles one of the C₄N rings of a porphyrin is exchanged against another moiety, and the resulting N,N,N-coordination pattern of transition metal ions often enforces a close contact to additional sites of the macrocycle and unusual bonding situations.

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Tripyrrin (HTrpy) is formally derived from the macrocyclic parent porphyrin by the loss of one of the four C₄N rings.⁵ Chemically, however, the Trpy ligand differs largely from the porphyrin with respect to ligand stability and the open cis-situated coordination site at the central ion. Concerning the meridonal N,N,N coordination and the mono-anionic nature, the tripyrrin ligand is closely related to the class of pincer ligands⁶ and, in particular, bis(arylimino)-isoindoline (BAI) ligands.⁷ The major difference to the systems in this study appears to be the presence of two terminal methyl moieties which shield the one coordination site situated in the N₃M plane of a given complex.⁸ Earlier studies have shown that as a result of this steric constraint palladium(II) complexes of Trpy ligands are always distorted from a planar geometry⁹ and that tetracoordinate nickel(II) tripyrrins display a sterically induced high spin ground state despite an intermediately strong ligand field.¹⁰

The presence of two terminal methyl groups at the tripyrrin ligand framework usually limits the maximum coordination number of metallotripyrrins to five. The association of a fifth donor can, in principle, occur from either side of the tripyrrin plane, resulting in two different coordination geometries **A** and **B** (Figure 2). Both forms have occasionally been observed on nickeltripyrins before.^{10,11} Two strategies have been applied in order to obtain the structurally distinct pentacoordinate tripyrrinates, the addition of donor ligands or solvents to metallotripyrrins TrpyMX to form species of

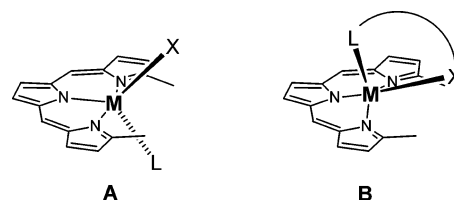


Figure 2. Generalized structures **A** and **B** for pentacoordinate metallotripyrrins.

the relaxed geometry **A** and the reaction with chelate ligands to form species of the strained geometry **B**.

Besides the preparative difficulties, the chemistry of metallotripyrrins has been largely hampered in the past by the sensitivity of the tripyrrolic moieties toward nucleophiles. So far, the synthesis of tripyrrin ligands has had to be carried out in strongly acidic media, and the metalation processes have basically consisted of competition reactions between the binding of excess protons or the transition metal ions at low pH.⁸ These conditions rendered the preparation of many metallotripyrrins almost impossible, especially those with labile complex fragments like TrpyCo, TrpyFe, or TrpyMn. In order to expand tripyrrin chemistry to these ions a new metalation procedure had to be sought. We report here a successful attempt and present a first study of Co^{II}, Fe^{II}, and Mn^{II} tripyrrins.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. TrpyNiNCO precursors **1** and **2** were prepared as previously described.¹² NMR spectra were obtained on a Bruker AMX 400 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (¹H spectra) or chloroform (¹³C). EI mass spectra were recorded on a Finnigan 90 MAT instrument. Values of m/z are given for the most abundant isotopes only. UV–vis data was collected on a Shimadzu UV-1601 PC spectrophotometer. IR spectra were obtained in Nujol paste on a Bruker Vector 22. Superconducting quantum interference device (SQUID) measurements were performed on a Quantum Design MPMS R2 magnetometer.

Demetalation of TrpyNiNCO 1 and 2 and Preparation of Free Base Tripyrrins 3 and 4—General Procedure: TrpyNiNCO **1** or **2** (0.1 mmol) is dissolved in diethyl ether (40 mL) and treated with a saturated aqueous KCN solution (10 mL) at ambient temperature in an ultrasound bath for 2 h. During this time, the color of the mixture changes from green to red. After phase separation the organic layer is washed with water (2 × 20 mL) and dried with sodium sulfate, resulting in a red ethereal solution of **3** or **4**, which is used directly for further reactions. For spectroscopic characterization small aliquots of these solutions were employed without further purification.

3,8,9,13-Tetraethyl-2,4,13,15-tetramethyltripyrin (3): MS (70 eV, EI) $m/z = 391$ (M⁺); UV–vis (Et₂O) λ_{max} (ϵ_{rel}) = 260 (0.58), 330 (1.75), 530 sh (1.06), 551 (1.13), 601 sh (0.31), 660 nm (0.49).

3,4,8,9,13,14-Hexaethyl-2,15-dimethyltripyrin (4): MS (70 eV, EI) $m/z = 419$ (M⁺); UV–vis (Et₂O) λ_{max} (ϵ_{rel}) = 263 (0.56), 334 (1.52), 530 sh (0.98), 554 (0.97), 605 sh (0.28), 662 nm (0.44).

Metalation of Free Base Tripyrrins and Formation of TrpyMX—General Procedure: Due to the oxygen sensitivity of

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the products, all steps have to be performed under a blanket of argon. The ethereal solution of **3** or **4** from above (0.1 mmol, calculated on the basis of 100% demetalation) is treated with water (30 mL) and a saturated solution of the desired metal(II) acetate hydrate in methanol (5 mL). After the solution is stirred for 30 min at ambient temperature, the color gradually changes to blue-green. The phases are separated, and the organic layer is washed with water (2 × 10 mL), a saturated solution of the sodium or potassium salt of the desired external ligand X (3 × 10 mL), and again with water (2 × 10 mL). If the product precipitates, it is filtered from the mixture, washed with water and diethyl ether, and dried in vacuo. For soluble products the organic layer is dried with sodium sulfate and then evaporated to dryness, and the residue is recrystallized from dichloromethane/*n*-hexane at 4 °C.

Acetato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)cobalt(II) (5). Prepared from **3** and cobalt(II) acetate (46.6 mg, 92%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = -5.1 (s, 6 H), 6.5 (s, 4 H), 7.0 (s, 6 H), 7.9 (s, 2 H), 12.9 (s, 6 H), 13.4 (s, 4 H), 65.7 (s, 3 H), 68.5 (s, 6 H); MS (EI, 70 eV) *m/z* = 446 ([M - OAc]⁺); IR (Nujol) 1 598, 1 567 cm⁻¹ (ν_{C=O}, ν_{C=C}); UV-vis (CH₂Cl₂) λ_{max} (ε) = 285 (22 000), 354 (51 200), 645 sh (27 100), 690 nm (40 300 mol⁻¹ dm³ cm⁻¹). Anal. Calcd for C₂₈H₃₇CoN₃O₂: C 66.39, H 7.36, N 8.30. Found: C 66.09, H 7.07, N 8.69.

Nitrato-(3,4,8,9,13,14-hexaethyl-2,15-dimethyltripyrinato)cobalt(II) (9). Prepared from **4**, cobalt(II) acetate, and potassium nitrate (45.1 mg, 89%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = -3.7 (s, 6 H), 7.4 (s, 6 H), 9.1 (s, 2 H), 10.2 (s, 4 H), 11.1 (s, 6 H), 11.6 (s, 6 H), 17.2 (s, 4 H), 44.8 (s, 4 H); MS (EI, 70 eV) *m/z* = 475 ([M - NO₃]⁺); UV-vis (CH₂Cl₂) λ_{max} (ε) = 283 (24 000), 355 (53 000), 420 sh (14 000), 650 sh (29 000), 686 nm (42 000 mol⁻¹ dm³ cm⁻¹). Anal. Calcd for C₂₈H₃₈CoN₄O₃: C 62.56, H 7.13, N 10.42. Found: C 62.32, H 7.03, N 10.18.

Chloro-(3,4,8,9,13,14-hexaethyl-2,15-dimethyltripyrinato)cobalt(II) (10). Prepared from **4**, cobalt(II) acetate, and sodium chloride (45.0 mg, 88%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = 1.4 (s, 6 H), 7.9 (s, 2 H), 10.0 (s, 6 H), 15.9 (s, 6 H), 16.8, 19.7 (2 × s, 4 H), 22.6, 24.4 (2 × s, 4 H), 35.8 (s, 6 H), 53.0, 59.4 (2 × s, 4 H); MS (EI, 70 eV) *m/z* = 475 ([M - Cl]⁺). Anal. Calcd for C₂₈H₃₈ClCoN₃: C 65.81, H 7.50, N 8.22. Found: C 65.48, H 7.56, N 7.96.

Iodo-(3,4,8,9,13,14-hexaethyl-2,15-dimethyltripyrinato)cobalt(II) (11). Prepared from **4**, cobalt(II) acetate, and sodium iodide (54.8 mg, 91%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = -1.38 (s, 6 H), 7.04 (s, 2 H), 7.82 (s, 6 H), 14.25 (s, 6 H), 15.57, 17.11 (2 × s, 4 H), 20.86, 22.21 (2 × s, 4 H), 31.29 (br s, 6 H), 56.48, 60.92 (2 × s, 2 H); MS (EI, 70 eV) *m/z* = 475 ([M - I]⁺). Anal. Calcd for C₂₈H₃₈ICoN₃: C 55.82, H 6.36, N 6.97. Found: C 55.75, H 6.24, N 6.74.

Isocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)cobalt(II) (12). Prepared from **3**, cobalt(II) acetate, and sodium cyanate (16.2 mg, 33%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = 0.1 (s, 6 H), 5.5 (s, 6 H), 9.9, 13.4 (2 × s, 4 H), 20.0 (s, 2 H), 22.6, 24.5 (2 × s, 4 H), 36.6 (s, 6 H), 76.7 (s, 6 H); MS (EI, 70 eV) *m/z* = 446 ([M - NCO]⁺); IR (Nujol) 2 210 (ν_{NCO}), 1 587 cm⁻¹ (ν_{C=N}); UV-vis (CH₂Cl₂) λ_{max} (ε) = 285 (21 200), 355 (46 000), 645 sh (22 800), 690 nm (36 400 mol⁻¹ dm³ cm⁻¹); UV-vis (acetone) λ_{max} (ε) = 347 (68 900), 600 sh (38 100), 642 nm (53 600 mol⁻¹ dm³ cm⁻¹); UV-vis (MeOH) λ_{max} (ε) = 270 (19 900), 347 (54 200), 610 sh (32 300), 650 nm (44 100 mol⁻¹ dm³ cm⁻¹). Anal. Calcd for C₂₇H₃₄CoN₄O: C 66.25, H 7.00, N 11.45. Found: C 65.90, H 6.87, N 11.07.

Isothiocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)cobalt(II) (13). Prepared from **3**, cobalt(II) acetate, and

potassium thiocyanate (43.5 mg, 86%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = 0.8 (s, 6 H), 5.4 (s, 6 H), 12.0, 15.0 (2 × s, 4 H), 20.6 (s, 2 H), 25.1, 27.2 (2 × s, 4 H), 38.9 (s, 6 H), 76.6 (s, 6 H); MS (EI, 70 eV) *m/z* = 475 ([M - NCS]⁺); IR (Nujol) 2 068 (ν_{NCS}), 1 577 cm⁻¹ (ν_{C=N}); UV-vis (CH₂Cl₂) λ_{max} (ε) = 285 (22 700), 355 (47 100), 650 sh (23 700), 688 nm (37 000 mol⁻¹ dm³ cm⁻¹). Anal. Calcd for C₂₇H₃₄CoN₄S: C 64.14, H 6.78, N 11.08. Found: C 63.88, H 6.89, N 10.88.

Isocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)iron(II) (14). Prepared from **3**, iron(II) acetate, and sodium cyanate (27.2 mg, 56%) as a violet solid: MS (EI, 70 eV) *m/z* = 443 ([M - NCO]⁺); IR (Nujol) 2203 (ν_{NCO}), 1 604 cm⁻¹ (ν_{C=N}); UV-vis (MeOH) λ_{max} (ε_{rel}) = 343 (0.44), 413 (0.12), 603 (0.34), 647 nm (0.60). Anal. Calcd for C₂₇H₃₄FeN₄O: C 66.67, H 7.05, N 11.52. Found: C 66.39, H 6.79, N 11.41.

Isothiocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)iron(II) (15). Prepared from **3**, iron(II) acetate, and potassium thiocyanate (22.1 mg, 44%) as a violet solid: MS (EI, 70 eV): *m/z* = 443 ([M - NCS]⁺); IR (Nujol) 2 055 (ν_{NCS}), 1 609 cm⁻¹ (ν_{C=N}). Anal. Calcd for C₂₇H₃₄FeN₄S: C 64.54, H 6.82, N 11.15. Found: C 64.49, H 6.60, N 10.77.

Isocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)manganese(II) (16). Prepared from **3**, manganese(II) acetate, and sodium cyanate (19.4 mg, 40%) as a violet solid: MS (EI, 70 eV) *m/z* = 442 ([M - NCO]⁺); IR (Nujol) 2 196 (ν_{NCO}), 1 596 cm⁻¹ (ν_{C=N}); UV-vis (CH₂Cl₂) λ_{max} (ε_{rel}) = 283 (0.16), 353 (0.36), 400 sh (0.11), 620 sh (0.15), 668 nm (0.23); UV-vis (acetone) λ_{max} (ε_{rel}) = 273 (0.12), 347 (0.36), 410 sh (0.09), 600 sh (0.18), 636 nm (0.29); UV-vis (MeOH) λ_{max} (ε_{rel}) = 270 (0.10), 347 (0.40), 411 (0.06), 599 (0.21), 640 nm (0.37). Anal. Calcd for C₂₇H₃₄MnN₄O: C 66.76, H 7.05, N 11.53. Found: C 66.90, H 7.00, N 11.22.

Isothiocyanato-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)manganese(II) (17). Prepared from **3**, manganese(II) acetate, and potassium thiocyanate (32.6 mg, 65%) as a violet solid: MS (EI, 70 eV) *m/z* = 442 ([M - NCS]⁺); IR (Nujol) 2 065 (ν_{NCS}), 1 598 cm⁻¹ (ν_{C=N}). Anal. Calcd for C₂₇H₃₄MnN₄S: C 64.65, H 6.83, N 11.17. Found: C 64.28, H 7.01, N 10.84.

Dicyanamido-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)cobalt(II) (18). Prepared from **3**, cobalt(II) acetate, and sodium dicyanamide (44.2 mg, 86%) as a violet solid: ¹H-NMR (CD₂Cl₂) δ = 1.6 (s, 6 H), 5.7 (s, 6 H), 15.0 (s, 4 H), 20.5 (s, 2 H), 26.6 (s, 4 H), 37.1 (s, 6 H), 74.6 (s, 6 H); MS (EI, 70 eV) *m/z* = 446 ([M - NCNCN]⁺); IR (Nujol) 2 316, 2 245, 2 183 (ν_{CN}), 1 599 cm⁻¹ (ν_{C=N}). Anal. Calcd for C₂₈H₃₄CoN₆: C 65.49, H 6.67, N 16.36. Found: C 65.09, H 6.77, N 16.07.

Dicyanamido-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)iron(II) (19). Prepared from **3**, iron(II) acetate, and sodium dicyanamide (40.8 mg, 80%) as a violet solid: MS (EI, 70 eV) *m/z* = 443 ([M - NCNCN]⁺); IR (Nujol) 2 318, 2 248, 2 181 (ν_{CN}), 1 593 cm⁻¹ (ν_{C=N}). Anal. Calcd for C₂₈H₃₄FeN₆: C 65.88, H 6.71, N 16.46. Found: C 65.91, H 6.78, N 16.09.

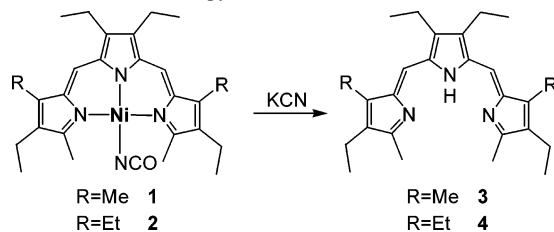
Dicyanamido-(3,8,9,14-tetraethyl-2,4,13,15-tetramethyltripyrinato)manganese(II) (20). Prepared from **3**, manganese(II) acetate, and sodium dicyanamide (41.8 mg, 82%) as a violet solid: MS (EI, 70 eV) *m/z* = 442 ([M - NCNCN]⁺); IR (Nujol) 2 315, 2 243, 2 172 (ν_{CN}), 1 587 cm⁻¹ (ν_{C=N}). Anal. Calcd for C₂₈H₃₄MnN₆: C 66.00, H 6.73, N 16.49. Found: C 65.61, H 6.69, N 16.22.

X-ray Analyses. X-ray quality crystals of TrpyCoI (**11**), TrpyCoNCO (**12**), TrpyCoNCS (**13**), TrpyCoNO₃ (**9**), and (TrpyFeNCO)₂O (**14**) were grown by diffusion on pentane into a dichloromethane solution at 4 °C. Crystallographic data for all compounds is given in Table 1. The ethyl group C20,C21 in the structure of

Table 1. Crystallographic Data for the Complexes **9**, **11**, **12**, **13**, and **14'**

	TrpyCoI (11)	TrpyCoNCO (12)	TrpyCoNCS (13)	TrpyCoNO ₃ (9)	(TrpyFeNCO) ₂ O (14')
formula	C ₂₈ H ₃₈ CoIN ₃	C ₂₇ H ₃₄ CoN ₄ O	C ₂₇ H ₃₄ CoN ₄ S	C ₂₈ H ₃₈ CoN ₄ O ₃	C ₅₄ H ₆₈ N ₈ Fe ₂ O ₃
fw	602.44	489.51	505.57	537.56	988.86
<i>a</i> / Å	10.5956(9)	11.0670(6)	10.972(3)	10.926(2)	18.9641(14)
<i>b</i> / Å	11.6384(10)	10.6803(6)	11.257(2)	11.574(2)	14.0552(16)
<i>c</i> / Å	12.4709(10)	20.8687(12)	20.908(8)	11.876(2)	19.4466(14)
α / deg	110.484(1)			82.30(3)	
β / deg	95.676(1)	97.148(1)	98.24(4)	67.94(3)	95.337(9)
γ / deg	102.899(1)			88.86(3)	
<i>Z</i>	2	4	4	2	4
<i>D</i> / g cm ⁻³	1.452	1.329	1.314	1.295	1.269
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
diffractometer	Bruker Smart Apex	Bruker Smart Apex	IPDS1 (Stoe)	IPDS1 (Stoe)	IPDS1 (Stoe)
radiation	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
monochromator	graphite	graphite	graphite	graphite	graphite
crystal size / mm	0.22 × 0.16 × 0.14	0.26 × 0.17 × 0.07	0.26 × 0.20 × 0.12	0.36 × 0.18 × 0.14	0.14 × 0.07 × 0.04
temperature / K	173(2)	173(2)	193(2)	193(2)	193(2)
data collection	ω -scan	ω -scan	ϕ -scan	ϕ -scan	ϕ -scan
Θ -range / deg	1.94–26.04	1.97–25.35	1.97–25.97	2.40–25.96	1.57–25.35
<i>h</i> -range	−13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13	−22 ≤ <i>h</i> ≤ 22
<i>k</i> -range	−14 ≤ <i>k</i> ≤ 14	−12 ≤ <i>k</i> ≤ 12	−13 ≤ <i>k</i> ≤ 13	−14 ≤ <i>k</i> ≤ 14	−16 ≤ <i>k</i> ≤ 16
<i>l</i> -range	−15 ≤ <i>l</i> ≤ 15	−25 ≤ <i>l</i> ≤ 25	−25 ≤ <i>l</i> ≤ 25	−14 ≤ <i>l</i> ≤ 14	−23 ≤ <i>l</i> ≤ 23
measured reflns	22367	23749	19737	13618	38292
indep reflns ^a	5354	3951	2441	4312	3442
abs. coefficient	1.763	0.728	0.775	0.657	0.612
struct solution ^b	Patterson	direct	direct	Patterson	Patterson
final <i>R</i> ₁ value	0.0271	0.0401	0.0457	0.0338	0.0402
final <i>R</i> ₂ value	0.0639	0.1003	0.0748	0.0880	0.0520

^a $I > 2\sigma(I)$. ^b All structures were solved using *SHELXS*, Program for Crystal Structure Determination¹³ and refined with *SHELXL*, Program for Crystal Structure Refinement.¹⁴

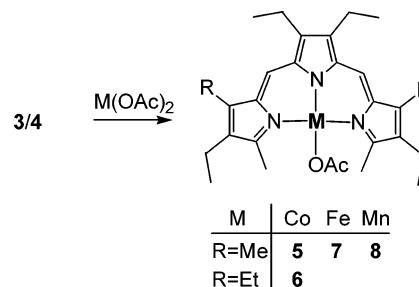
Scheme 1. Preparation of Free Base Tripyrins **3** and **4** by KCN-Induced Demetalation of TrpyNiNCO **1** and **2**

14' was found to occupy two positions in a ratio of 68.08:31.92 and was therefore treated with an appropriate disorder model.

Results and Discussion

Preparation of Free Base Tripyrins and Insertion of Co^{II}, Fe^{II}, and Mn^{II}. Although the action of nucleophiles on metallotripyrins usually leads to the immediate decomposition of the compound,^{8–11} the treatment of TrpyNiNCO chelates **1** and **2**¹² with an aqueous solution of excess potassium cyanide is an exception and results in a clean demetalation. The tripyrins **3** and **4**, which are obtained after phase separation as the free base ligands in etheral solutions, decompose over the course of 2 h under standard conditions, so all attempts to isolate pure compounds failed. For this reason only, a limited set of reliable spectroscopic data from MS and UV–vis measurements have been obtained so far (Scheme 1).

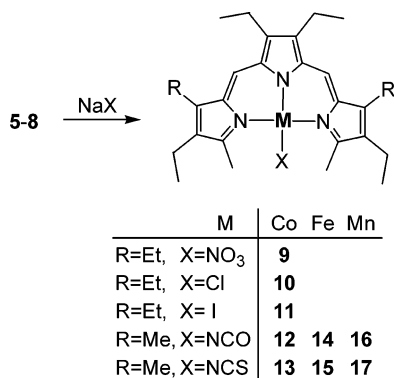
The advent of the free base ligands **3** and **4** opens the possibility of obtaining more sensitive complexes unavailable by other means. For the metalation of free base tripyrins, a two-phase system with the ligand in the etheral phase and an acetate salt of Co^{II}, Fe^{II}, or Mn^{II} in the aqueous phase

Scheme 2. Preparation of Acetato Complexes **5–8** via Free Base Tripyrins **3** and **4**

was applied (Scheme 2). Some methanol was added to ensure the interpenetration of the two layers and thus to enhance the metalation rate. No additional base is necessary to drive the metalation to completion. Since the removal of the solvent often leads to the decomposition of sensitive metallotripyrins, the product solutions of the assumed acetato species TrpyCoOAc (**5** and **6**), TrpyFeOAc (**7**), and TrpyMnOAc (**8**) were used in ligand exchange reactions without further purification. As shown below, the attempted isolation of these complexes was in fact successful only for the cobalt chelate **5**. The same holds true for the structurally similar nitrate species, which were prepared from **6**, **7**, and **8** by ligand exchange with sodium nitrate (Scheme 3) and of which only the cobalt derivative **9** could be isolated and analyzed further.

The isolated compounds **5** and **9** were analyzed by mass spectra (TrpyCo⁺ signal) and by microanalyses. Solution magnetic moments of **5** and **9** were determined to $\mu_{\text{eff}} = 4.6 \pm 0.1$ and $4.7 \pm 0.1 \mu_{\text{B}}$, respectively, using the Evans method.¹⁵ These values are in agreement with the assignment of **5** and **9** to high spin Co^{II} species. In addition, **5** and **9**

Scheme 3. Preparation of Metallotripyrrins TrpyMX **9–17** with M = Co^{II}, Fe^{II}, and Mn^{II} and X = NO₃, Cl, I, NCO, and NCS via Anion Metathesis Reactions



show very similar ¹H NMR and UV–vis spectroscopic patterns (see Experimental Section), which suggest that the anion binding mode of both complexes and therefore the structural type with respect to Figure 2 is the same.

TrpyCoNO₃ (**9**) was characterized structurally and recognized as prototype for a four-membered ring O,O-chelate metallotripyrrin of geometry **B**. The result of the X-ray crystallographic analysis is presented in Figure 3. Selected molecular data and details of the structure solution and refinement are summarized in Tables 1 and 2. The molecular structure of **9** is determined largely by a close-to-planar C₁₄N₃ perimeter with atoms deviating from the mean plane by a maximum of 0.0784(19) Å. The cobalt(II) ion binds to the tripyrrin with a doming of 0.5348(2) Å and with Co–N distances of 1.9734(17)–2.0122(16) Å. This results in N–Co–N angles of 92.51(7)°, 92.68(7)°, and 145.99(6)° and in a distance of 4.240(3) Å between the methyl termini. The nitrate anion is bound to the Co^{II} ion via O1 and O2 with distances of 2.0479(15) and 2.3832(17) Å and an angle O–Co–O of 57.42(6)°. This nonsymmetric coordination leads to a nitrate ion with three different N4–O distances, of which the N4–O1 bond is noticeably longer (1.283(2) Å) than the other two. O2 is presumably only weakly attracted by the cobalt(II) ion. The coordination geometry at the central ion is strongly distorted and can be assigned to a square pyramidal form with O1 in the apical position as well as to a trigonal bipyramidal one with N2 and O2 as the apexes. For both limiting conformations the bond angles found in the central CoN₃O₂ unit deviate significantly from ideal values. In addition, neither of these geometries provides an explanation for the largely nonsymmetrical binding mode of the nitrate ligand of **9**. Another unexpected result comes from an analysis of intramolecular strain. The distance between O2 and the terminal methyl group C1H₃ undercuts the sum of the van der Waals radii by as much as 14.9%. Furthermore, this strain is not released by a diminished N2–Co–O1 angle. The unusual coordination of the nitrate ion in **9** has a precedent in the nickel(II) series.¹²

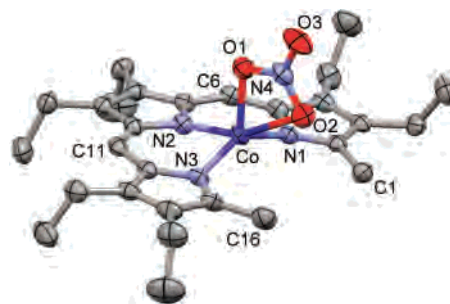


Figure 3. Molecular structure of TrpyCoNO₃ (**9**) (ellipsoids at 50% probability, hydrogen atoms omitted for clarity).

Preparation and Characterization of TrpyMX (X = NO₃, Cl, I, NCO, NCS). In general, a wide range of tetracoordinate metallotripyrrins TrpyMX can be obtained by different ligand exchange procedures.^{9,10} In this study the simple extraction of an etheral solution of the respective precursor acetato complex **5–8** with an aqueous solution of excess salt NaX was used to attempt the introduction of nitrate as well as the halide and pseudohalide ions chloride, iodide, cyanate, and thiocyanate (Scheme 3).

The desired TrpyMX complexes initially formed in all cases, but decomposition was observed in the case of nitrate-, chlorido-, and iodidoiron(II) and manganese(II) chelates. Combustion analyses were used to confirm the composition of the isolated complexes. Compounds **9–17** are readily soluble in most organic solvents. The new compounds are very air-sensitive, especially in solution, and react with dioxygen in seconds (TrpyFeX), minutes (TrpyMnX), or hours (TrpyCoX). Susceptibility measurements in CD₂Cl₂ solution were carried out using the Evans method.¹⁶ At room temperature, the cobalt complexes **10**, **11**, **12**, and **13** gave μ_{eff} values of 4.4 ± 0.1 , 4.6 ± 0.1 , 4.7 ± 0.1 , and 4.4 ± 0.1 μ_{B} , respectively. These data are typical for paramagnetic d⁷ cobalt(II) with $S = 3/2$ and proof the presence of the expected high spin configuration of the ion. For the more sensitive iron and manganese compounds **14–17** the results of several measurements deviated strongly, so no secure spin-state assignment was possible. The mass spectra of **9–17** are dominated by strong signals from the cationic TrpyM⁺ fragments, and the anionic coligands could not be recorded for any of the compounds. ¹H NMR spectroscopic measurements were hampered by the line broadening due to the paramagnetic nature of the complexes and, even more severely, by the pronounced sensitivity of the compounds under the study toward dioxygen. Reliable and reproducible spectra were only obtained from cobalt derivatives. These spectra show the expected paramagnetic shifts in the range

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complexes **9**, **11–13**, and **14'**

	TrpyCoNO ₃ (9)	TrpyCoI (11)	TrpyCoNCO (12)	TrpyCoNCS (13)	(TrpyFeNCO) ₂ O (14')
M–N1	2.0112(16)	1.9982(18)	2.0072(19)	2.000(3)	2.132(3)
M–N2	1.9734(17)	1.9648(17)	1.9710(17)	1.967(3)	2.038(3)
M–N3	2.0122(16)	2.0062(18)	2.0160(19)	1.994(3)	2.116(3)
M–D1 ^a	2.0479(15)	2.5921(3)	1.988(2)	1.959(3)	1.981(4)
M–D2 ^a	2.3832(17)				1.787(3)
N1–M–N2	92.51(7)	92.60(7)	92.11(7)	92.99(13)	89.17(12)
N1–M–N3	145.99(6)	140.85(8)	142.12(7)	146.06(13)	173.92(12)
N1–M–D1 ^a	108.70(6)	105.95(5)	103.64(8)	101.04(13)	87.73(14)
N1–M–D2 ^a	91.81(6)				93.36(12)
N2–M–N3	92.68(7)	92.83(7)	92.23(7)	92.92(12)	88.96(12)
N2–M–D1 ^a	101.10(7)	123.85(5)	127.49(8)	125.52(13)	118.87(15)
N2–M–D2 ^a	158.26(6)				117.11(13)
N3–M–D1 ^a	103.20(6)	102.89(5)	103.28(8)	102.49(13)	88.10(14)
N3–M–D2 ^a	95.58(6)				92.64(12)
D1–M–D2 ^a	57.42(6)				124.02(15)
X–D1 ^a	1.283(2)		1.097(3)	1.180(5)	1.149(5)
X–D2 ^a	1.248(2)				
X–Y ^a	1.228(2)		1.217(4)	1.589(4)	1.219(5)
D1–X–D2 ^a	116.24(16)				
D1–X–Y ^a	121.00(18)		179.4(3)	178.3(4)	177.5(5)
D2–X–Y ^a	122.8(2)				
C1⋯C16	4.240(3)	4.073(4)	4.123(3)	4.179(6)	4.935(6)
C1⋯D1 ^a	4.504(3)	4.156(2)	3.709(3)	3.660(6)	3.290(6)
C1⋯D2 ^a	3.022(3)				3.419(5)
C16⋯D1 ^a	4.405(3)	4.144(3)	3.741(3)	3.673(5)	3.223(5)
C16⋯D2 ^a	3.131(3)				3.461(5)
Δ _{vdW} /% ^b	–14.9	+4.1	+4.5	+3.1	–9.3
M⋯Ct(N ₃) ^c	0.5348(2)	0.6033(3)	0.5952(3)	0.5254(5)	0.1089(6)

^a D1 = O1 (**9**), I (**11**), N4 (**12**, **13**), N7 (**14'**); D2 = O2 (**9**), O3 (**14'**); X = N4 (**9**), C27 (**12**, **13**, **14'**); Y = O3 (**9**), O (**12**), S (**13**), O1 (**14'**). ^b Difference between the closest C1⋯D1/2 or C16⋯D1/2 distance and the sum of the van der Waals radii of D1/2 and the closest terminal methyl group. ^c Displacement of the metal ion from the N,N,N plane of the tripyrrin ligand (doming).

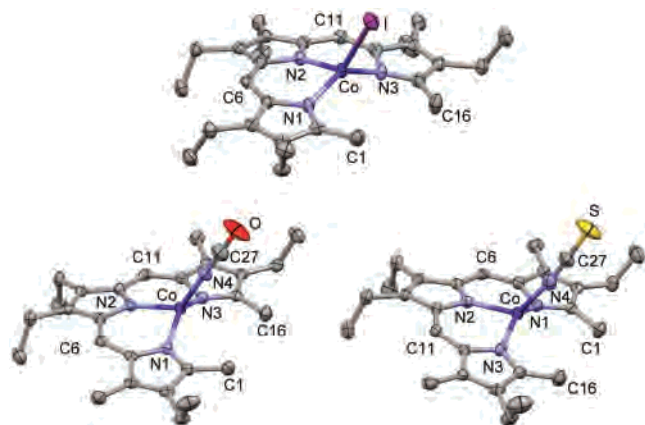


Figure 4. Molecular structures of the tetracoordinate TrpyCoI (**11**), TrpyCoNCO (**12**), and TrpyCoNCS (**13**) (ellipsoids at 50% probability, hydrogen atoms omitted for clarity).

of –1.5 to +77 ppm and diastereotopically split ABX₃ systems for the chemically distinct ethyl groups, which indicate the presence of an axial ligand on one side of the Trpy plane.

Crystallographic studies were performed on the cobalt species **11**, **12**, and **13** (Figure 4, Table 1 and 2) and on the iron isocyanato derivative **14'** (see below, Figure 5 and Tables 1 and 2). As a common feature to the molecular structures in this series of cobalt(II) chelates the cobalt(II) ions are coordinated in a strongly distorted tetrahedral environment and the tripyrrin ligand appears to be rather invariant with respect to the in-plane geometry. Indicative for the latter is the observation that all N1–M–N2 and N2–M–N3 angles are found in the narrow range of 92.11–

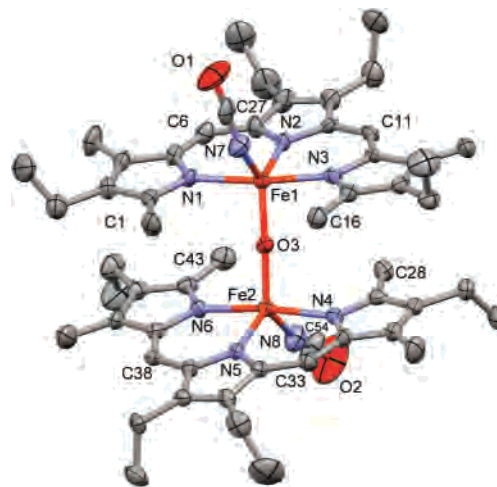


Figure 5. Molecular structure of **14'** (ellipsoids at 50% probability, hydrogen atoms omitted for clarity).

92.92° and that the terminal methyl groups C1H₃ and C16H₃ are situated at an intramolecular distance of 4.073–4.179 Å, which is close to the van der Waals limit of 4.0 Å. The size of the anionic coligands of **11–13** seems to have only little influence on the structure of the cobalttripyrrins. Within this series the only arrangements observed are those in which the donor center, by which the anionic ligand is bound to the transition metal ion, is situated in an unstrained manner above the methyl termini with a deviation from the van der Waals limit of less than 5%. The analysis of the molecular structures shows that other than for tetracoordinate nickel(II) tripyrrins,^{10–12} the molecular arrangements of tetracoordinate cobalt(II) tripyrrins TrpyMX are mainly a con-

sequence of the rigid and inflexible tripyrrin backbone and of purely steric factors like ion radii and van der Waals contacts. Intramolecular strains and stresses, which should be associated with deviations from electronically favored coordination geometries, cannot be observed within the CoN₃D fragments of **11–13** and are presumably compensated for by the tripyrrolic framework.

Attempts to crystallize the iron or manganese tripyrrins **14–17** were not successful. These compounds were found to be extremely sensitive with respect to dissociation as well as oxidation, so long-term crystallization attempts usually resulted in the decomposition of the material. In one instance, however, the slow crystallization of a TrpyFeNCO derivative (obtained from **7** and sodium cyanate using the standard procedure) from a methanol-containing mixture of CH₂Cl₂ and *n*-hexane at 4 °C yielded a small amount of dark violet crystals of **14'**. **14'** decomposes rapidly upon dissolution, so no reliable spectroscopic measurement could be conducted. Only the presence of a TrpyFe subunit could be proven by a signal at *m/z* 444 in the EI mass spectrum of **14'**. All attempts to prepare **14'** selectively also failed because of the instability of the compound. Fortunately, the crystals obtained were suitable for X-ray diffraction, and the crystallographic analysis revealed that neither the expected TrpyFeNCO species **14** nor a methanol adduct or a cationic TrpyFe-(MeOH)₂⁺ complex is present, but the μ -oxo derivative **14'**, which must have formed from TrpyFeNCO and a small amount of dioxygen, was present. Crystallographic data and selected molecular parameters for **14'** are summarized in Tables 1 and 2, respectively. Each molecule of **14'** contains two crystallographically nonequivalent but structurally similar TrpyFeNCO fragments. Only data from the TrpyFe1 fragment is given in the table. Figure 5 shows the molecular structure of **14'**.

The iron atoms Fe1 and Fe2 are both coordinated by four nitrogen and one oxygen donor in a close-to-ideal trigonal bipyramidal fashion, with N1,N3 and N4,N6 in the respective apical positions. The equatorial planes are occupied by N2, N7, and O3 on Fe1 and N5, N8, and O3 on Fe2. The largest deviations from ideal angles are found within the TrpyFe fragments at N1–Fe1–N3 and N4–Fe2–N6, which are as small as 174°. All other N–Fe–N and N–Fe–O angles within the coordination unit deviate from the ideal 90° or 120° by less than 4°.

The Fe–N bond lengths within the TrpyFe subunits of **14'** differ from each other by as much as 0.1 Å and are smaller for the central Fe–N2 bond than for the terminal Fe–N1/N3 bonds. In addition, the Fe–N bonds of **14'** are long as compared to those for tetracoordinate TrpyCoX species. The atom Fe1 is moved out of the mean N1,N2,N3 plane toward the other iron ion Fe2 by a comparatively small value of only 0.1089(6) Å. Finally, the tripyrrin ligand is stretched to a C_{term}···C_{term} distance of 4.935(6) Å in order to provide sufficient space for the coordination of the Fe ion. All these data are typical for pentacoordinate metallotripyrrins of geometry **A**.

As expected, the isocyanate ligands coordinate via the N-atoms in distances of 1.981(4) and 1.971(4) Å to Fe1 and

Fe2, respectively, and display binding angles Fe–N–C of 151.51(14)° for Fe1 and 168.13(14)° for Fe2. The distances between the N_{NCO} and the C_{term} centers are surprisingly small and undercut the van der Waals distance by as much as 9.3%. The intramolecular strain that should result from this arrangement may be one underlying reason for the unexpectedly high reactivity and low stability of **14'**.

Both iron atoms Fe1 and Fe2 are bound to the oxygen atom O3 in distances of 1.787(3) and 1.782(3) Å, respectively. The Fe–O–Fe subunit is almost linear with an angle of 175.12(17)° and thus similar to those of many μ -oxo iron porphyrins.¹⁶ From a sterical point of view, the TrpyFe subunits are left with only a very limited number of possible low-energy arrangements and are therefore rotated by 170.9-(2)° and arranged almost coplanar with an angle of only 4.2-(2)° between the mean planes.

Donor Association Studies: Formation of Coordination Polymers. Solvent addition was studied on TrpyMNCO species with M = Co (**12**), Fe (**14**), and Mn (**16**) using UV–vis spectroscopy. The spectra of these species were measured at room temperature in three different solvents (CH₂Cl₂, acetone, MeOH), using concentrations of approximately 10^{–6} mol L^{–1}. (Figure 6). All TrpyMNCO compounds show characteristic strong absorptions between 300 and 800 nm. In analogy to the porphyrins, one intense absorption is always present in the high-frequency part of the spectra at about 350 nm, accompanied by a number of bands between 500 and 750 nm.

In the nickel series the transition from a tetracoordinate species in dichloromethane solution to a pentacoordinate one is accompanied by an increase in the intensities of the low-energy bands and an additional hypsochromic shift.¹² With the use of these observations as criteria for solvent coordination, the spectra show the formation of associates from cobalt(II) and manganese(II) complexes **12** and **16** with acetone and methanol at the chosen concentrations. On the other hand, dilute solutions of the iron(II) compound **14** appear too instable for reliable measurements in dichloromethane as well as in acetone. Only the spectra taken in methanol solutions were reproducible. However, the spectral pattern observed for **14** as well as the relatively low wavelength of the most intense Q-type band at 647 nm suggests the formation of a cationic methanol adduct TrpyFe-(MeOH)₂⁺ also for iron.

In the nickel series we have recently shown that pentacoordinate tripyrrins tend to form 1D coordination polymers of type **A** with pseudohalide ligands. The thiocyanato and dicyanamido (dca) ligands proved particularly useful as bridging moieties.¹² Besides the crystallographic evidence, IR spectroscopic investigations in Nujol paste gave insight in the binding mode of the pseudohalide anion and thus in the degree of aggregation (monomeric vs polymeric) of the compounds of interest.¹⁷

As depicted in Scheme 4, the dca derivatives TrpyCodca (**18**), TrpyFedca (**19**), and TrpyMndca (**20**) were obtained

(17) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B; John Wiley & Sons: New York, 1997; p 105.

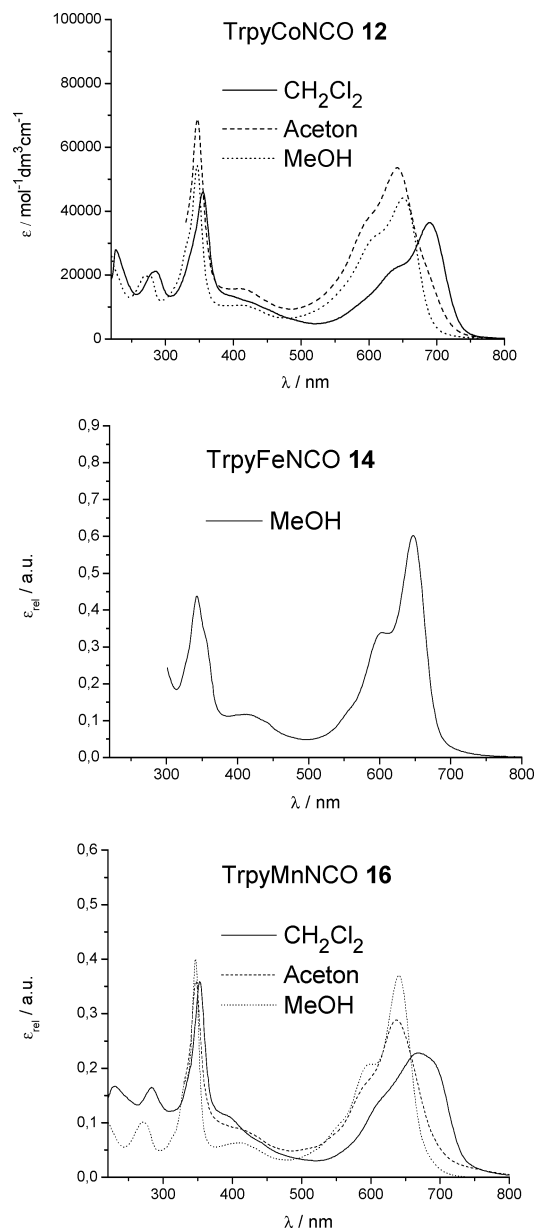
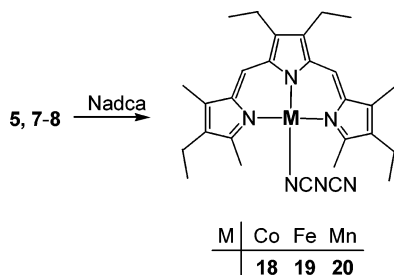


Figure 6. UV-vis spectra of **12** (top) and **16** (bottom) in dichloromethane, acetone, and methanol solution and of **14** (middle) in methanol solution.

Scheme 4. Preparation of Metallotripyrins TrpyMdca **18–20** with $M = \text{Co}^{\text{II}}$, Fe^{II} , and Mn^{II}



from the acetates **5**, **7**, and **8** by simple ligand exchange procedures with sodium dicyanamide. The new derivatives are only slightly soluble in the reaction mixture and separate directly after the addition of the pseudohalide anion. Isolation was accomplished by filtration and excessive washing of the precipitates, and the composition TrpyMdca was confirmed

Table 3. Selected IR Absorptions of Pseudohalide Complexes **13**, **15**, and **17–20** in cm^{-1}

complex	ν (cm^{-1})
NCS derivatives	
TrpyCoNCS (13)	2068
TrpyFeNCS (15)	2055
TrpyMnNCS (17)	2065
dca derivatives	
TrpyCodca (18)	2316, 2245, 2183
TrpyFedca (19)	2318, 2248, 2181
TrpyMndca (20)	2315, 2243, 2172

by elemental analysis in all cases. Investigations of the degree of association were performed by vibrational spectroscopy. Table 3 summarizes characteristic IR data for the pseudohalide complexes TrpyMNCS and TrpyMdca **13**, **15**, and **17–20**.

All three complexes with the NCS ligand **13**, **15**, and **17** show CN stretching bands below 2100 cm^{-1} , which is typically a sign for an end-on binding mode of the N-bound pseudohalide, and are thus in agreement with the result from the X-ray diffraction study on the cobalt derivative **13**. For the complexes with the dicyanamide ligands **18–20**, three stretching vibrations are observed, of which the signal at highest energy is assigned to the $\nu_s + \nu_{as}$ combination band of the CN moieties. This band is characteristic for the coordination mode of the dca ligand in that an end-on coordination is indicated by wavenumbers below 2290 cm^{-1} , whereas for a 1,5-bridging coordination mode the wavenumber is usually at or above 2300 cm^{-1} .¹⁷ Clearly, the latter scenario is the case here, and **18–20** thus have to be addressed as 1D coordination polymers.

Since no suitable crystals for a single-crystal structure determination study of the dca complexes could be obtained, the new polymers were further characterized by SQUID measurements. Magnetic susceptibility measurements for **18–20** were carried out at saturation magnetization (applied field of $30\,000 \text{ G}$ for **18** and $10\,000 \text{ G}$ for **19** and **20**) in the temperature range from 2 to 300 K . Figure 7 shows the development of the product $\chi_M T$ and of χ^{-1} with temperature for **18**, **19**, and **20**.

All complexes show a similar temperature dependence of the magnetic susceptibility. For **18**, **19**, and **20** the $\chi_M T$ values at 300 K are 2.587 , 3.835 , and $5.089 \text{ cm}^3 \text{ K mol}^{-1}$ and prove the presence of high spin cobalt(II), iron(II), and manganese(II) ions, respectively, at this temperature. As the temperature is lowered the $\chi_M T$ values decrease continuously, slowly at first and then faster upon cooling below 50 K , reaching values of 0.652 (**18**), 1.174 (**19**), and $1.377 \text{ cm}^3 \text{ K mol}^{-1}$ (**20**) at 2 K . This behavior indicates very weak antiferromagnetic interactions between the spin centers, presumably by coupling through the 1,5- μ -dca bridges.

The χ_M^{-1} versus T plots of **18–20** were fitted to the Curie–Weiss law in the temperature range of $2–300 \text{ K}$ with $C = 2.659$, 3.862 , and $5.088 \text{ cm}^3 \text{ K mol}^{-1}$ and with $\theta = -9.98$, -7.27 , and -8.20 K , respectively. A weak antiferromagnetic interaction is typical for 3d transition metal compounds with bridging dca ligands.¹⁸ Although the devia-

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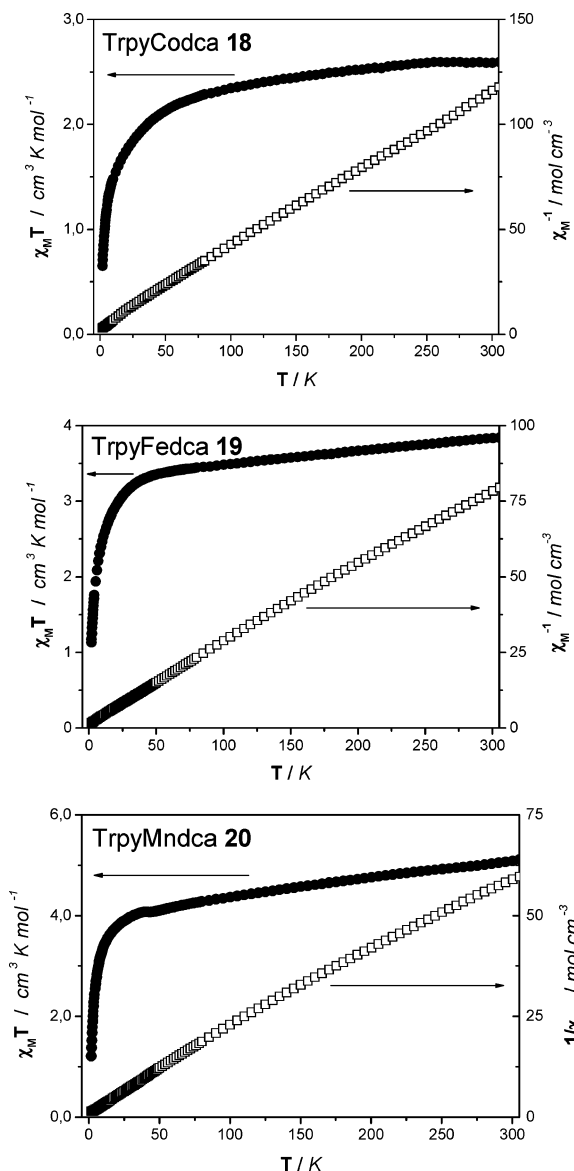


Figure 7. Thermal variation of the product $\chi_M T$ (●) and of χ^{-1} (□) for **18** (top), **19** (center), and **20** (bottom).

tions from the Curie–Weiss law, which are particularly obvious for **20**, indicate a more complex magnetic behavior of 1D polymeric metallotripyrrins, the results from the susceptibility measurements support the assignment of **18**–**20** to 1D polymeric structures.

Conclusions

We have reported a first-principles study on sensitive cobalt, iron, and manganese tripyrrin complexes that were made available via the selective action of cyanide on nickel chelates TrpyNiNCO. All three ions form normal N,N,N bound TrpyMX complexes with an intermediately strong propensity for the association of a fifth donor. The tetra-coordinate tripyrrins of Co^{II} , Mn^{II} , and especially Fe^{II} are very sensitive to air, particularly in solution, and clean samples of the latter two could only be obtained with the anionic cyanato and thiocyanato external ligands. X-ray crystallographic work proved the presence of unstrained tetra-coordinate species for cobalt(II) and the formation of pentacoordinate species in either of the two coordination modes that had been shown as characteristic of TrpyM fragments. Despite their pronounced sensitivity the new TrpyM fragments can be used to build coordination polymers. As an example, dicyanamido derivatives of the tripyrrin complexes of all three metal ions yield insoluble and much less sensitive materials with interesting magnetic properties. We are currently exploiting this opportunity and use the new TrpyM fragments for the construction of metal–organic frameworks and the like.

Besides this material scientific aspect it should be noted that tetra-coordinate iron and manganese complexes exist with the closely related *p*- and *m*-benzporphyrins as well as with N-confused porphyrins.^{1,2,4} However, other than in tetra-coordinate metallotripyrrins, the highly reactive and Lewis acidic open sites at the transition metal ion of these compounds are sterically blocked by favorably situated aromatic moieties. Therefore, strong noncovalent interactions between the unsaturated metal ions and the aromatic group can be anticipated in particular with these ions. In fact, agostic interactions, selective oxidative transformations, and a number of spectroscopic peculiarities have recently been found and studied in these systems.

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Supporting Information Available: CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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