

ELECTRONIC SUPPLEMENTARY INFORMATION

for

Rendering Classical Hydrophilic Enantiopure Werner Salts $[M(en)_3]^{n+}$
 nX^- Lipophilic ($M/n = Cr/3, Co/3, Rh/3, Ir/3, Pt/4$); New Chiral
Hydrogen Bond Donor Catalysts and Enantioselectivities as a Function
of Metal and Charge

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Experimental Section (continued)

Δ -[Cr(en)₃]³⁺ 3BAr_f⁻. Δ -[Cr(en)₃]³⁺ 3Cl⁻·1.6H₂O (0.0228 g, 0.0620 mmol),^{s1} H₂O (15 mL), CH₂Cl₂ (15 mL), and Na⁺ BAr_f⁻ (0.1650 g, 0.1861 mmol) were combined in a procedure analogous to that for Λ -[Cr(en)₃]³⁺ 3BAr_f⁻. An identical workup gave Δ -[Cr(en)₃]³⁺ 3BAr_f⁻·14H₂O as a canary yellow solid (0.1742 g, 0.05667 mmol, 91%) that was stored at -35 °C to slow decomposition. Anal. Calcd. for C₁₀₂H₆₀B₃CrF₇₂N₆·14H₂O (3074.17): C 39.85, H 2.89, N 2.73; found C 40.04, H 2.71, N 2.49. The thermal behavior and IR and UV-vis spectra were identical to those of the enantiomer (*see experimental procedure in the main text*).

Δ -[Co(en)₃]³⁺ 3BAr_f⁻. A round bottom flask was charged with a colorless solution of Na⁺ BAr_f⁻ (0.494 g, 0.557 mmol) in CH₂Cl₂ (25 mL). Then a solution of Δ -[Co(en)₃]³⁺ 3I⁻·H₂O^{s2} (0.119 g, 0.186 mmol) in water (20 mL) was added. The heterogeneous mixture was vigorously stirred for 10 min. The now orange CH₂Cl₂ phase was separated from the aqueous phase and the CH₂Cl₂ was allowed to evaporate in a fume hood overnight to give Δ -[Co(en)₃]³⁺ 3BAr_f⁻·14H₂O as an orange solid (0.501 g, 0.163 mmol, 87%). Anal. Calcd. for C₁₀₂H₆₀B₃CoF₇₂N₆·14H₂O (3081.07): C, 39.76; H, 2.88; N, 2.73; found: C, 39.87; H, 2.77; N, 2.66. The thermal behavior and NMR (¹H, ¹³C{¹H}), IR, and UV-vis spectra were identical to those of the enantiomer (*see experimental procedure in the main text*).

Δ -[Rh(en)₃]³⁺ 3BAr_f⁻. Δ -[Rh(en)₃]³⁺ 3Cl⁻·2.3H₂O (0.0204 g, 0.0473 mmol),^{s1b} H₂O (10 mL), CH₂Cl₂ (10 mL), and Na⁺ BAr_f⁻ (0.1257 g, 0.1418 mmol) were combined in a procedure analogous to that for Λ -[Rh(en)₃]³⁺ 3BAr_f⁻. An identical workup gave Δ -[Rh(en)₃]³⁺ 3BAr_f⁻·11.5H₂O as an ivory solid (0.1407 g, 0.04568 mmol, 97%), Anal. Calcd. for C₁₀₂H₆₀B₃F₇₂N₆Rh·11.5H₂O (3080.04): C 39.78, H 2.72, N 2.73; found C 40.25, H 2.68, N 2.73. The thermal behavior and NMR (¹H, ¹³C{¹H}), IR, and UV-vis spectra were identical to those of the enantiomer (*see experimental procedure in the main text*).

Δ -[Ir(en)₃]³⁺ 3BAr_f⁻. Δ -[Ir(en)₃]³⁺ 3Cl⁻·2H₂O (0.0236 g, 0.0458 mmol),^{s3} H₂O (15 mL), CH₂Cl₂ (15 mL), and Na⁺ BAr_f⁻ (0.1219 g, 0.1376 mmol) were combined in a procedure analogous to that for Λ -[Ir(en)₃]³⁺ 3BAr_f⁻. An identical workup gave Δ -[Ir(en)₃]³⁺ 3BAr_f⁻·9-

H₂O as a white solid (0.1391 g, 0.04452 mmol, 97%). Anal. Calcd. for C₁₀₂H₆₀B₃F₇₂·IrN₆·9H₂O (3124.31): C 39.21, H 2.52, N 2.69; found C 39.10, H 2.53, N 2.72. The thermal behavior and NMR (¹H, ¹³C{¹H}), IR, and UV-vis spectra were identical to those of the enantiomer (*see experimental procedure in the main text*).

Δ -[Pt(en)₃]⁴⁺ 4BAr_f⁻. Δ -[Pt(en)₃]⁴⁺ 4Cl⁻·2H₂O (0.0180 g, 0.0325 mmol),^{s4} H₂O (10 mL), CH₂Cl₂ (10 mL), and Na⁺ BAr_f⁻ (0.1153 g, 0.1301 mmol) were combined in a procedure analogous to that for Λ -[Pt(en)₃]⁴⁺ 4BAr_f⁻. An identical workup gave Δ -[Pt(en)₃]⁴⁺ 4BAr_f⁻·17H₂O as a pale yellow solid (0.1280 g, 0.03096 mmol, 95%). Anal. Calcd. for C₁₃₄H₇₂B₄F₉₆·N₆Pt·17H₂O (4134.52): C 38.93, H 2.58, N 2.03; found C 39.05, H 2.48, N 2.02. The thermal behavior and NMR (¹H, ¹³C{¹H}), IR, and UV-vis spectra were identical to those of the enantiomer (*see experimental procedure in the main text*).

Thermal experiments (Table 1). A. An open capillary was charged with *ca.* 0.008 g of the salt and inserted into an Optimelt MPA 100 instrument. The sample was heated from 30.0 °C to the temperature listed in column 3 of Table 1 at 10.0 °C/min, and then allowed to cool to room temperature before dissolution in acetone-*d*₆ for ¹H NMR analysis. **B.** The other experiments employed either a TA Instruments Q50 TGA, using 0.010-0.015 g samples that were heated from 30.0 to 500.0 °C at 10.0 °C/min, or a TA Instruments Q20 DSC, using 0.005-0.010 g samples that were heated from 25.0 °C to 50 °C beyond their liquefaction temperature at 10.0 °C/min.

References

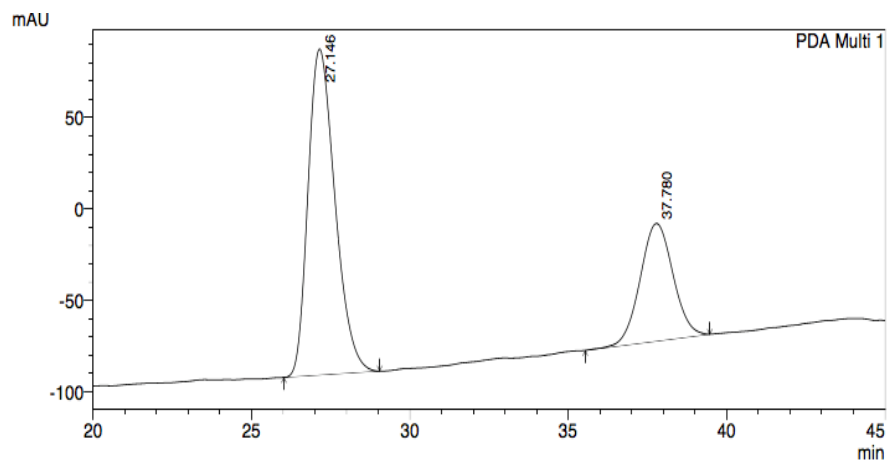
(s1) (a) Gillard, R. D.; Mitchell, P. R. Tris(diamine)chromium(III) Salts. *Inorg. Synth.* **1972**, *13*, 184-186. (b) Galsbøl, F. Resolution of Tris(ethylenediamine)-rhodium(III) and -chromium(III) Chloride by Means of (+)-Tartrate. *Inorg. Synth.* **1970**, *12*, 269-280.

(s2) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. Resolution of the Tris(ethylenediamine)cobalt(III) Ion. *Inorg. Synth.* **1960**, *6*, 183-186.

(s3) Galsbøl, F.; Rasmussen, B. S. The preparation, resolution, and characterization of tris(1,2-ethanediamine)iridium(III) complexes. *Acta Chem. Scand.* **1982**, *A36*, 83-87.

(s4) (a) Werner, A. Über Spiegelbildisomerie bei Platinverbindungen I. *Vierteljahresschr. Naturforsch. Ges. Zürich* **1917**, *62*, 553-564. (b) Giedt, D. C.; Nyman, C. J. Tris(ethylenediamine)platinum(IV) Chloride. *Inorg. Synth.* **1966**, *8*, 239-241.

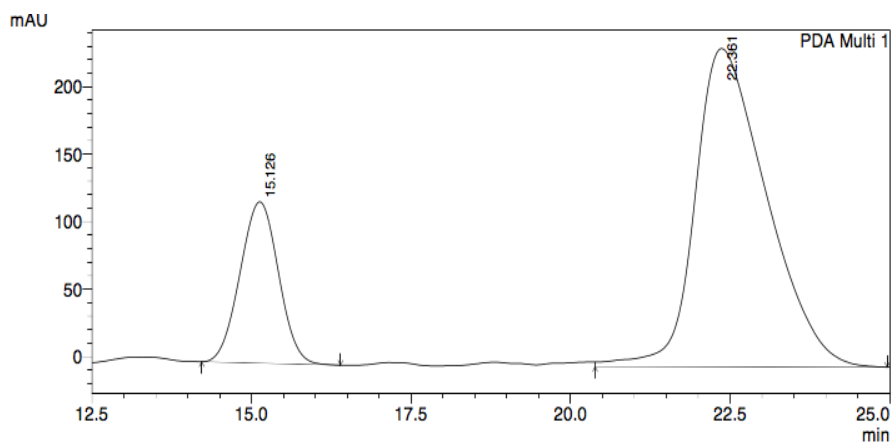
Representative HPLC traces used for determination of ee values.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.146	10569265	178400	69.453	73.470
2	37.780	4648531	64420	30.547	26.530
Total		15217796	242820	100.000	100.000

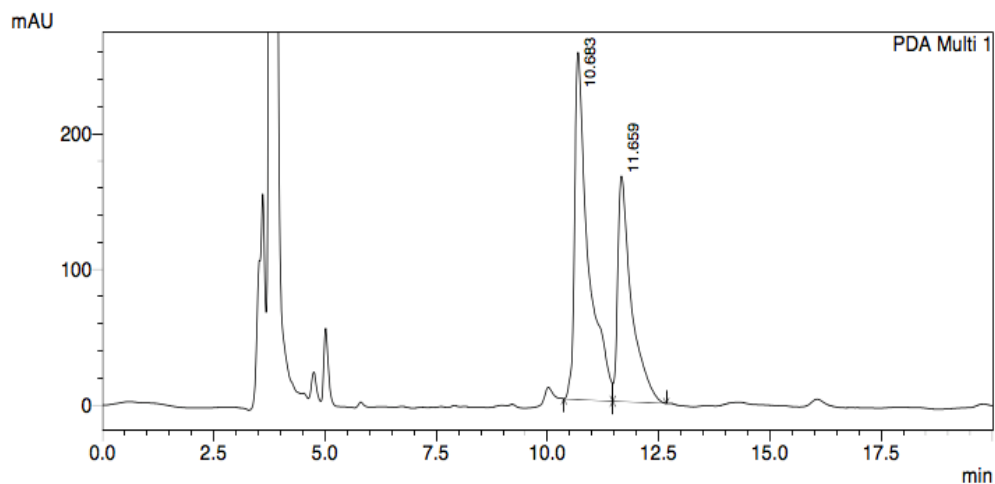
Figure s1. HPLC trace for **1** in Chart 1, entry 5.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.126	5007507	119434	21.386	33.636
2	22.361	18406889	235643	78.614	66.364
Total		23414395	355077	100.000	100.000

Figure s2. HPLC trace for **2** in Chart 2, entry 5.



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.683	5453817	255985	60.376	60.643
2	11.659	3579281	166131	39.624	39.357
Total		9033098	422116	100.000	100.000

Figure s3. HPLC trace for **3** in Chart 3, entry 6.

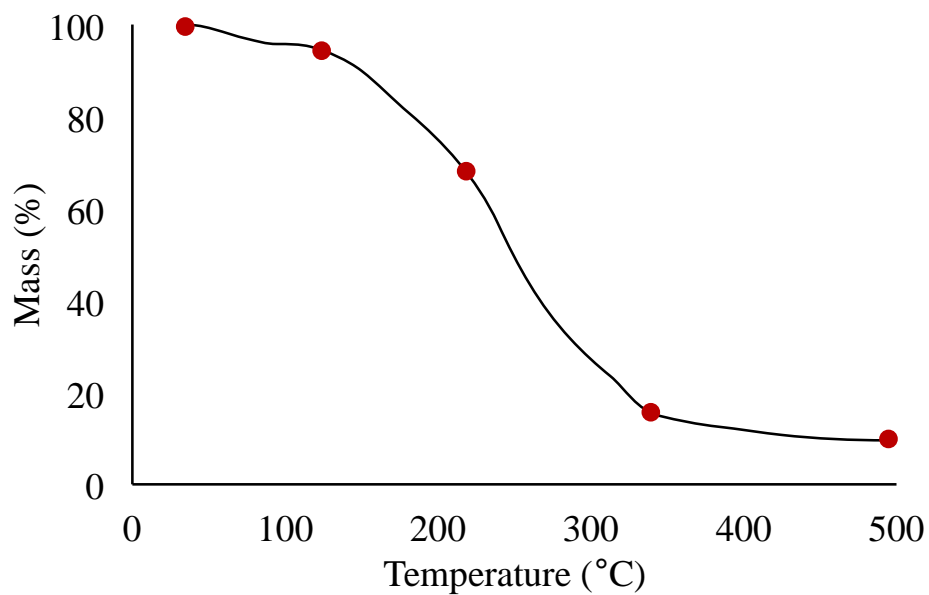


Figure s4. TGA trace for Λ -[Cr(en)₃]³⁺ 3BAR_f⁻.

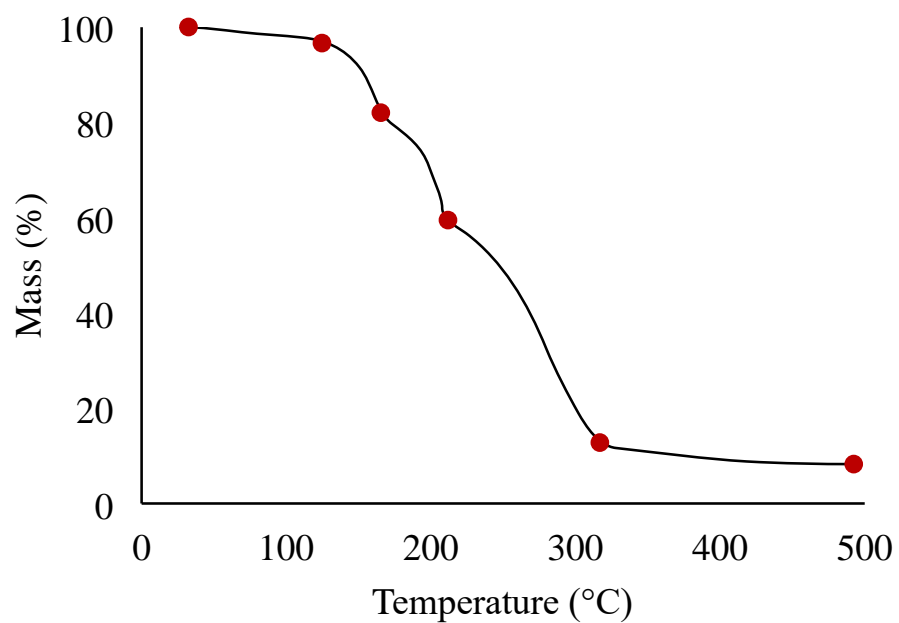


Figure s5. TGA trace for Λ -[Co(en)₃]³⁺ 3BARF⁻.

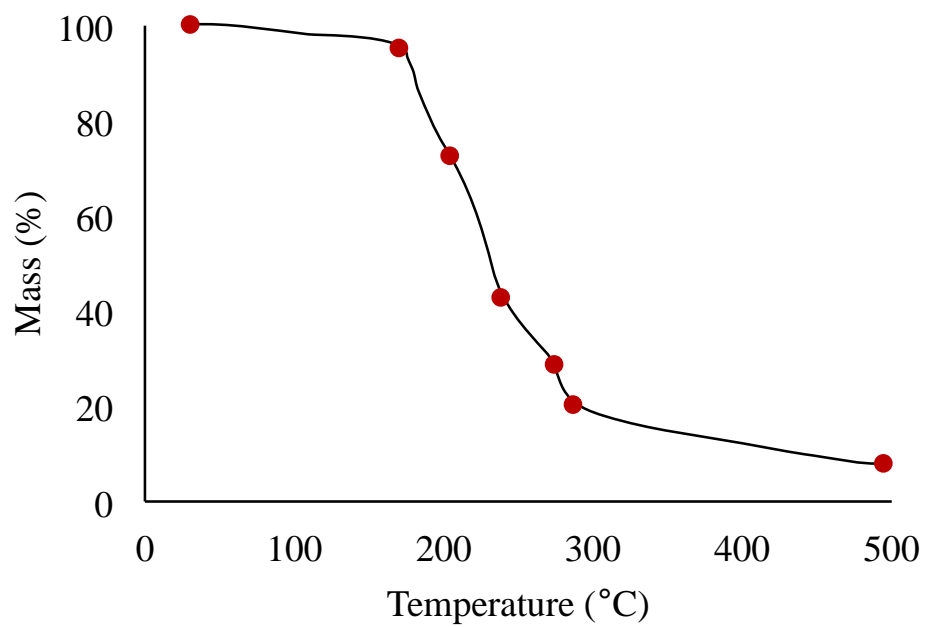


Figure s6. TGA trace for Λ -[Rh(en)₃]³⁺ 3BARF⁻.

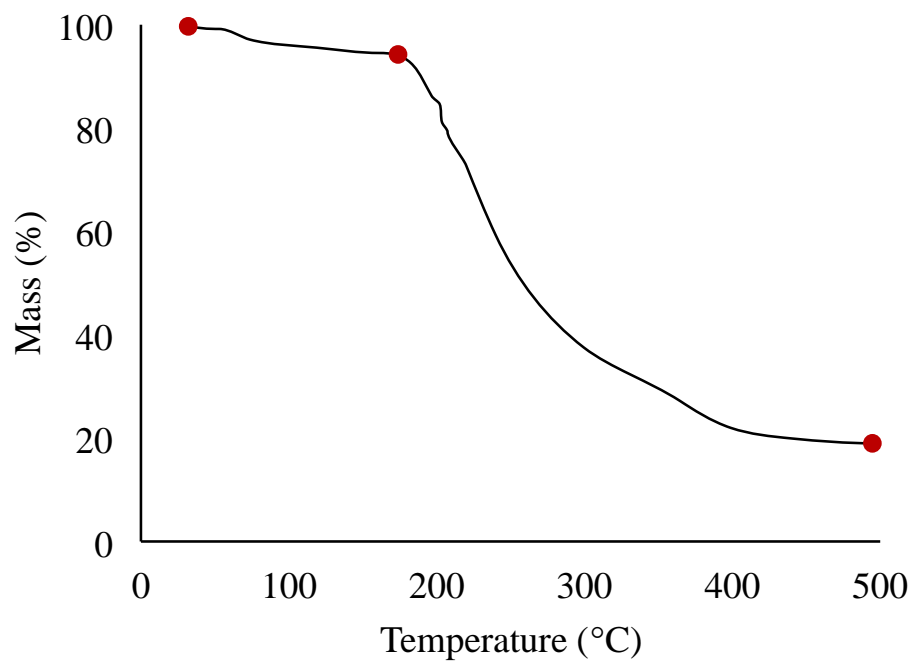


Figure s7. TGA trace for Λ -[Ir(en)₃]³⁺ 3BAR_f⁻.

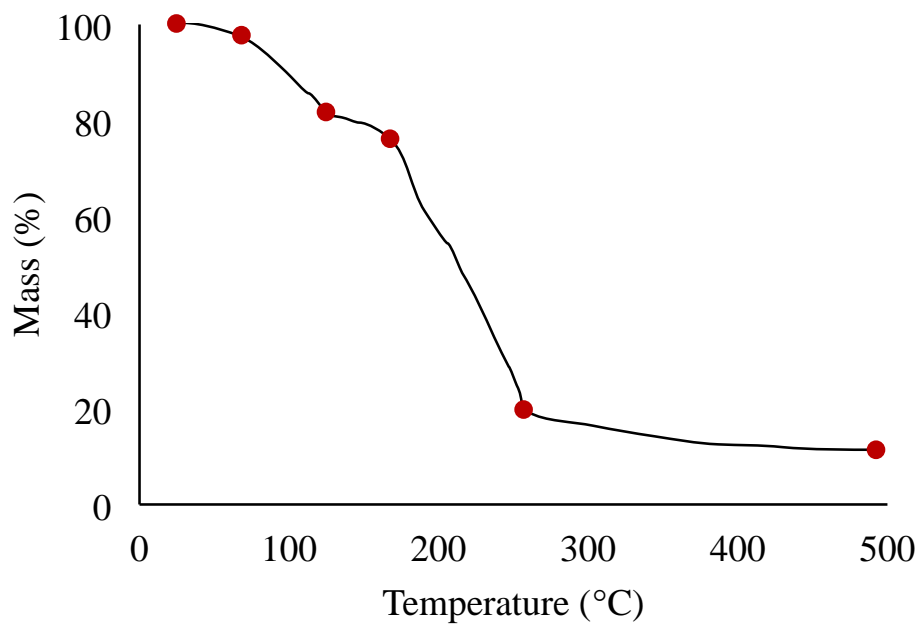


Figure s8. TGA trace for Λ -[Pt(en)₃]⁴⁺ 4BAR_f⁻.

Table s1. Hydration levels (*z*) of isolated chloride and iodide salts $[M(en)_3]^{n+} nX^- \cdot zH_2O$.

M^{n+}	nX^-	<i>z</i>
<i>rac</i> -Cr(III)	3Cl ⁻	3 ^a
<i>rac</i> -Cr(III)	3Cl ⁻	3 ^b
Λ-Cr(III)	3Cl ⁻	1.6 ^c
Λ-Cr(III)	3Cl ⁻	2 ^b
<i>rac</i> -Cr(III)	3Cl ⁻	3.72 ^d
<i>rac</i> -Cr(III)	3I ⁻	0 ^b
<i>rac</i> -Co(III)	3Cl ⁻	4 ^d
<i>rac</i> -Co(III)	3Cl ⁻	2.8 ^b
Λ-Co(III)	3Cl ⁻	0 ^b
Λ-Co(III)	3I ⁻	1 ^e
<i>rac</i> -Co(III)	3I ⁻	1 ^b
<i>rac</i> -Co(III)	3I ⁻	0 ^f
Λ-Rh(III)	3Cl ⁻	2.3 ^g
<i>rac</i> -Rh(III)	3Cl ⁻	3.37 ^d
<i>rac</i> -Rh(III)	3I ⁻	0 ^f
Λ-Ir(III)	3Cl ⁻	2 ^g
<i>rac</i> -Ir(III)	3Cl ⁻	3.4 ^d
<i>rac</i> -Ir(III)	3I ⁻	0 ^f
<i>rac</i> -Pt(IV)	4Cl ⁻	2 ^h
<i>rac</i> -Pt(IV)	4Cl ⁻	2.5 ⁱ
<i>rac</i> -Pt(IV)	4Cl ⁻	0 ^j
<i>rac</i> -Pt(IV)	4I ⁻	0 ⁱ

^aGillard, R. D.; Mitchell, P. R. *Inorg. Synth.* **1972**, *13*, 184-186. ^bMiller, S. E.; House, D. A. *Inorg. Chim. Acta* **1989**, *157*, 29-32. ^cGalsbøl, F. *Inorg. Synth.* **1970**, *12*, 269-280. ^dTakamizawa, S.; Kohbara, M.; Akatsuka, T.; Miyake, R. *New J. Chem.* **2008**, *32*, 1782-1787. ^eBroomhead, J. A. Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183-186. ^fMoczygemba, G. A.; Lagowski, J. J. *J. Coord. Chem.* **1976**, *5*, 71-76. ^gGalsbøl, F.; Rasmussen, B. S. *Acta Chem. Scand.* **1982**, *A36*, 83-87. ^hGiedt, D. C.; Nyman, C. J. *Inorg. Synth.* **1966**, *8*, 239-241. ⁱWendlandt, W. *Texas J. Sci.* **1962**, *14*, 264-277. ^jHouse, J. E., Jr.; Tahir, F. M. *Thermochim. Acta* **1987**, *118*, 191-197.