

Syntheses, structures, and magnetic characterization of dicyanometalate(II) building blocks: $[\text{NEt}_4][(\text{Tp}^*)\text{M}^{\text{II}}(\text{CN})_2]$ [$\text{M}^{\text{II}} = \text{Cr}, \text{Co}, \text{Ni}$; $\text{Tp}^* = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$]

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The syntheses and structures of three dicyanometalate(II) complexes, $[\text{NEt}_4][(\text{Tp}^*)\text{M}^{\text{II}}(\text{CN})_2] \cdot n\text{MeCN} \cdot \frac{1}{2}\text{Et}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Cr}$, **1**, $n = \frac{1}{2}$; Co , **2**, $n = 1$; Ni , **3**, $n = 1$) are described; magnetic studies indicate that **3** is diamagnetic while **1** and **2** are paramagnetic high- and low-spin $S = 2$ and $\frac{1}{2}$ complexes, respectively.

Several cyanometalate complexes and networks that exhibit frequency dependent magnetic relaxation have been described over the last few years. These so-called single molecule- (SMM)^{1,2} and single-chain magnets (SCM)³ exhibit magnetic properties that are dominated by the single-ion anisotropy of the building blocks. We and others report that anisotropic cyanometalate building blocks with unquenched orbital angular momenta are necessary to construct complexes and networks that exhibit frequency-dependent magnetic relaxation behavior that is characteristic of SMM and SCM materials.^{1–3} To date relatively few cyanometalate-based analogues have been described, being limited to a few anisotropic metal centers (e.g. Fe^{III} , Mn^{III} , Mo^{III} and Re^{II}).^{1–3}

As part of a sustained effort to investigate the self-assembly of cyanometalate complexes into common structural archetypes, we have developed a general synthetic route for preparing well-defined and anisotropic di- and tricyanometalate complexes.² Following a building block synthetic approach, these discrete molecular precursors are allowed to self-assemble with structures intact into a common structural archetype, thus allowing for detailed structure–property relationships to be described; current efforts focus on probing relationships between molecular symmetry/shape anisotropy, spin–orbit coupling, π backbonding, and superexchange efficiency in magnetic and photoresponsive cyanometalate-based materials.²

Herein we describe the syntheses, structures, and magnetic characterization of three structurally similar divalent five coordinate dicyanometalates. Treatment of $[(\text{Tp}^*)\text{Cr}^{\text{III}}\text{Cl}_2(\text{THF})]^{+4}$ ($\text{Tp}^* = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$) with Na/Hg amalgam in tetrahydrofuran, followed by tetraethylammonium cyanide $[(\text{NEt}_4)\text{CN}]^{-5}$ in acetonitrile solution, affords $[\text{NEt}_4][(\text{Tp}^*)\text{Cr}^{\text{II}}(\text{CN})_2] \cdot \frac{1}{2}\text{MeCN} \cdot \frac{1}{2}\text{Et}_2\text{O}$ (**1**) as dichroic purple-orange crystals; **1** is the first example of a well-defined, high-spin

dicyanochromate(II) complex.[†] Additional analogues, $[\text{NEt}_4][(\text{Tp}^*)\text{M}^{\text{II}}(\text{CN})_2] \cdot \text{MeCN} \cdot \frac{1}{2}\text{Et}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Co}$, **2**; Ni , **3**), are obtained as orange crystals *via* treatment of $[(\text{Tp}^*)\text{M}^{\text{II}}(\text{OAc})\text{MeCN}]^6$ ($\text{M}^{\text{II}} = \text{Co}, \text{Ni}$) with $[\text{NEt}_4]\text{CN}^{\dagger}$

The infrared spectrum of **1** exhibits intense ν_{BH} (2515 cm^{-1}) and ν_{CN} (2103 cm^{-1}) stretching absorptions that are shifted to higher energies relative to a variety of cyanochromate salts. The ν_{CN} stretch in **1** is likely at higher energy than those found for $[\text{NEt}_4]_3[\text{Cr}^{\text{II}}(\text{CN})_5]^{7}$ (2086 cm^{-1}) and $\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]^{8}$ (2020 cm^{-1}) due to a lower overall charge.⁹ In comparison, the ν_{CN} stretches observed in $[\text{NEt}_4][(\text{Tp}^*)\text{Cr}^{\text{III}}(\text{CN})_3]^{2g}$ (2125 cm^{-1}), $[(\text{Me}_3\text{tacn})\text{Cr}^{\text{III}}(\text{CN})_3]^{10}$ (2133 cm^{-1}) ($\text{tacn} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$), and $\text{K}_3[\text{Cr}^{\text{III}}(\text{CN})_6]^{9,11}$ (2130 cm^{-1}) are found at higher energies, suggesting that Cr^{II} centers are present in **1**.

Infrared spectra obtained for **2** and **3** also exhibit intense, low-energy ν_{BH} and ν_{CN} absorptions, indicating that divalent metal centers are present. The ν_{BH} (2502 cm^{-1}) and ν_{CN} (2091 cm^{-1}) absorptions for **2** are shifted to lower energies relative to those in **1**, with the ν_{CN} stretch being comparable to those in $[(\text{triphos})\text{Co}^{\text{II}}(\text{CN})_2]^{12}$ (2096 cm^{-1}), $[\text{NBu}_4]_2[\text{Co}^{\text{II}}(\text{CN})_4(\text{py})]^{13}$ (2079 cm^{-1}), $\text{Li}_3[\text{Co}^{\text{II}}(\text{CN})_5]^{14}$ (2080 cm^{-1}), and $[\text{NBu}_4]_2[\text{Co}^{\text{II}}(\text{CN})_4]^{13}$ (2095 cm^{-1}). Consistent with the presence of Co^{II} centers, the ν_{CN} in **2** is lower in energy than those exhibited by $\text{K}_3[\text{Co}^{\text{III}}(\text{CN})_6]^{9,15}$ (2126 cm^{-1}), $[(\text{tacn})\text{Co}^{\text{III}}(\text{CN})_3]^{16}$ (2129 cm^{-1}), and $[\text{NEt}_4][(\text{Tp}^*)\text{Co}^{\text{III}}(\text{CN})_3]^{2g}$ (2131 cm^{-1}). Likewise, **3** exhibits low-energy ν_{BH} (2504 cm^{-1}) and ν_{CN} (2114 cm^{-1}) stretches, with the ν_{CN} being similar to those in $[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$ (2095, 2111, 2123 cm^{-1})¹⁷ and $[(\text{triphos})\text{Ni}(\text{CN})_2]^{18}$ (2165, 2105 cm^{-1}).

For compounds **1–3** the anions are essentially isostructural and crystallize in the monoclinic $P2_1/c$ space group.[†] The metal centers adopt distorted square pyramidal, C_s -symmetric $[\text{cis-M}^{\text{II}}(\text{CN})_2(\text{Tp}^*)]^{-}$ coordination geometries, where the two *cis*-pyrazoles (Tp^* ligand) and two cyanide ligands comprise the basal $\{\text{C}_2\text{N}_2\}$ plane (Fig. 1). The divalent metal centers are *ca.* 0.14, 0.61, and 0.08 Å above this $\{\text{C}_2\text{N}_2\}$ plane, while a third coordinated pyrazole is found at the apical site, with $\text{M}^{\text{II}}\text{–N}_5$ distances of 2.244(3), 2.100(3), and 2.389(2) Å found for **1–3**, respectively; we presume that the Jahn–Teller axis lies perpendicular to the basal plane and along the Cr1–N5 bond vector in **1** (Fig. 1).⁷

The M–C and M–N_{eq} bond lengths in **1–3** become shorter progressing from chromium to nickel. The average M–C and M–N_{eq} distances are 2.110(4) and 2.110(3) Å for **1**, 1.898(4) and 1.972(3) Å for **2**, and 1.853(3) and 1.935(2) Å for **3**, and are comparable to the average M–C bond lengths in $[\text{Cr}(\text{CN})_5]^{3-}$ [2.12(1) Å],⁷ $[(\text{triphos})\text{Co}(\text{CN})_2]$ [1.90(1) Å],¹² $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ [1.89(0) Å],¹⁷ and $[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$ [1.89(1) Å].¹⁷

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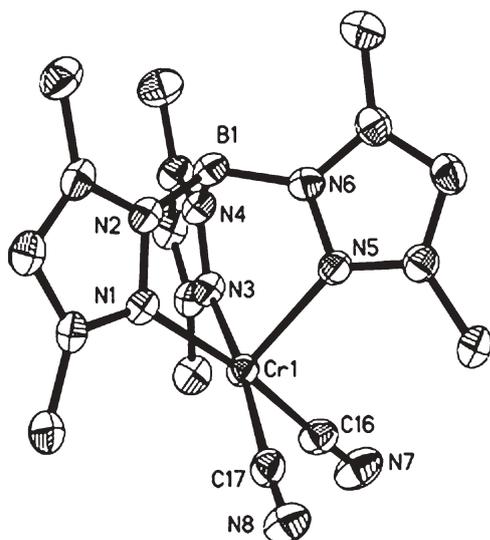


Fig. 1 X-Ray structure of **1**. Thermal ellipsoids are at the 50% level and all hydrogen atoms, lattice solvent, and cations are removed for clarity.

The M–C≡N angles are nearly linear, while the C16–M–C17 and N1–M–N3 angles decrease and increase, respectively, in **1–3** as a function of increasing metal electronegativity. The M–C16–N7 bond angles range from 176.9(3) to 178.0(3)°, while the C16–M–C17 bond angles become more acute progressing from 89.6(2)° for **1**, 88.7(2)° for **2**, to 86.4(2)° for **3**. Consistent with ionic radii trends, the N1–M–N3 angles concomitantly increase from 84.4(2), to 87.1(2), and 88.3(2)°, for **1–3**, respectively.¹⁸

The electronic spectra of **1–3** collected between 300 and 800 nm, exhibit low-intensity absorptions that are attributed to spin-allowed, Laporte-forbidden transitions within the 3d orbital manifold (Fig. 2). In acetonitrile (MeCN) solution, **1** exhibits overlapping low-intensity absorptions at 459 nm ($\epsilon_M = 50 \text{ M}^{-1} \text{ cm}^{-1}$) and 497 nm ($47 \text{ M}^{-1} \text{ cm}^{-1}$), in addition to a broad absorption near 612 nm ($17 \text{ M}^{-1} \text{ cm}^{-1}$); in comparison, $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$ exhibits a single broad absorption at 452 nm ($122 \text{ M}^{-1} \text{ cm}^{-1}$).⁷ For **2**, absorptions at 390 nm ($163 \text{ M}^{-1} \text{ cm}^{-1}$) and 688 nm ($14 \text{ M}^{-1} \text{ cm}^{-1}$) are found, while **3** exhibits a single transition at 391 nm ($118 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁹

Magnetic measurements clearly show that **3** is diamagnetic ($S = 0$), while **1** and **2** are paramagnetic high- ($S = 2$) and low-spin

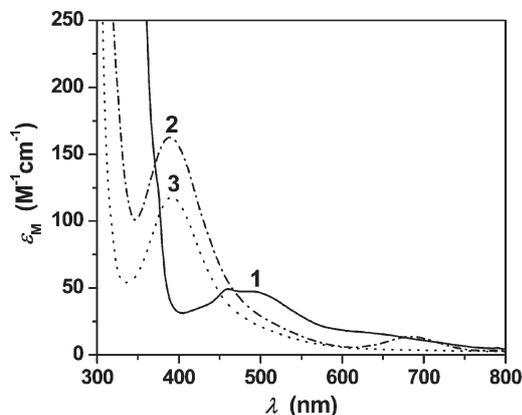


Fig. 2 Electronic absorption spectra of **1–3** in MeCN.

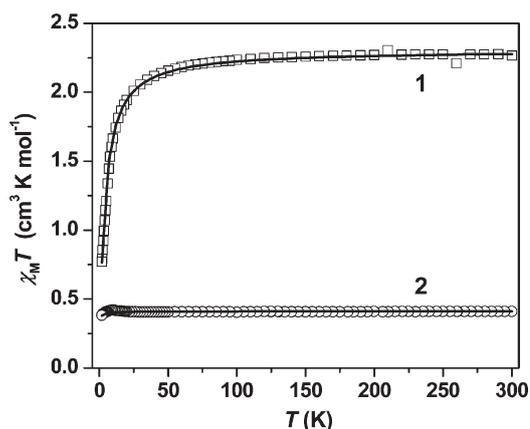


Fig. 3 χT vs. T data for **1** and **2** between 1.8 and 300 K ($H_{\text{dc}} = 1 \text{ kG}$). The solid lines represent least-squares fitting of the χT data.

($S = 1/2$) complexes, respectively (Fig. 3). For **1**, the χT product ($2.28 \text{ cm}^3 \text{ K mol}^{-1}$) remains nearly constant between 300 and 100 K, and dramatically decreases below *ca.* 20 K, towards a minimum value ($0.76 \text{ cm}^3 \text{ K mol}^{-1}$) at 1.8 K; for **2**, the χT product ($0.41 \text{ cm}^3 \text{ K mol}^{-1}$) remains constant between 300 and 10 K, and decreases slightly, towards $0.38 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. Fitting of the χT vs. T data *via* the Curie–Weiss expression affords g , Weiss (θ), and Curie (C) parameters of 1.77 and 2.12, -4.2 and -0.18 K , and 2.35 and $0.41 \text{ cm}^3 \text{ K mol}^{-1}$, for **1** and **2**, respectively.²⁰ Similar values have been found for $[(\text{triphos})\text{Co}(\text{CN})_2]^{12,21}$ and a series of compounds containing Cr^{II} centers,²² while the negative θ values exhibited by **1** and **2** are suggestive of intermolecular antiferromagnetic interactions.²⁰ For **2**, fitting of the M vs. H data using an $S = 1/2$ Brillouin function gives $g = 2.09$, which is close to the value obtained *via* Curie–Weiss fits of the χT vs. T data;²⁰ accurate fitting of the M vs. H data to an $S = 2$ Brillouin function for **1** presumably failed due to the presence of antiferromagnetic dipolar interactions. Hence, we propose that **1–3** exhibit $S = 2$, $1/2$, and zero ground states, respectively.

In summary, we have described the preparation, structures, and magnetic properties of three structurally related divalent poly(pyrazolyl)borate dicyanometalates. To our knowledge, **1–3** are rare examples of divalent five coordinate dicyanometalates, with **1** being the first example containing Cr^{II} centers. Future efforts will investigate the self-assembly of **1** and **2** into polynuclear cyanide-bridged magnetic complexes.

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Notes and references

† Synthesis of **1**: under an argon atmosphere, treatment of $[(\text{Tp}^*)\text{Cr}^{\text{III}}\text{Cl}_2(\text{THF})]$ (0.492 g, 1.00 mmol) with Na/Hg amalgam (0.023 g, 0.79%, 1.00 mmol) in THF (60 mL) with stirring afforded a pale blue suspension after 1 h. The blue mixture was transferred into a MeCN

(10 mL) solution of [NEt₄]CN (0.312 g, 2.00 mmol) and rapidly afforded a pale purple suspension. The mixture was allowed to stir an additional 30 min and was concentrated under vacuum to ca. 15 mL volume. The mixture was filtered and the purple filtrate was layered with Et₂O (30 mL) and allowed to stand for 7 d. Dichroic purple-orange needles were collected *via* filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum for 1 h at room temperature. Yield of **1**: 0.157 g (29.5%). Anal. Calcd for C₂₅H₄₂BCrN₉: C, 56.50; H, 7.97; N, 23.72. Found: C, 56.26; H, 8.21; N, 23.49%. IR (Nujol, cm⁻¹): 2515 (s), 2103 (s).

Synthesis of **2**: under an argon atmosphere, treatment of [(Tp*)Co^{II}(OAc)(MeCN)] (0.587 g, 1.00 mmol) with [NEt₄]CN (0.312 g, 2.00 mmol) in MeCN (10 mL) with stirring afforded an orange solution that was allowed to stir for 30 min. The mixture was layered with Et₂O (50 mL) and allowed to stand for 3 d. The orange rods were isolated *via* filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum for 1 h at room temperature. Yield of **2**: 0.364 g (67.6%). Anal. Calcd for C₂₅H₄₂BCoN₉: C, 55.77; H, 7.86; N, 23.41. Found: C, 55.77; H, 7.64; N, 23.25%. IR (Nujol, cm⁻¹): 2502 (s), 2091 (vs).

Synthesis of **3**: treatment of [(Tp*)Ni^{II}(OAc)(MeCN)] (0.587 g, 1.00 mmol) with [NEt₄]CN (0.312 g, 2.00 mmol) in MeCN (10 mL) with stirring afforded an orange solution that was allowed to stir for 30 min. The mixture was layered with Et₂O (60 mL) and allowed to stand for 3 d. The orange rods were isolated *via* filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum for 1 h at room temperature. Yield of **3**: 0.460 g (85.4%). Anal. Calcd for C₂₅H₄₂BNiN₉: C, 55.79; H, 7.87; N, 23.42. Found: C, 55.66; H, 7.86; N, 23.71%. IR (Nujol, cm⁻¹): 2504 (s), 2114 (s).

Crystallographic data for **1** was collected on a Bruker X8 Proteum rotating anode CCD diffractometer using graphite-monochromated Cu K α radiation. X-Ray data for **2** and **3** were collected on a Nonius-Kappa CCD diffractometer using Mo K α radiation. All structures were solved by direct methods and refined against all data using SHELXL-97.²³ Crystal data for **1**: C₂₈H_{48.5}BCrN_{9.5}O_{0.5}, *M* = 589.07, monoclinic, space group *P*2₁/*c*, *a* = 10.1192(3) Å, *b* = 13.9716(4) Å, *c* = 24.4089(7) Å, β = 91.565(2)°, *V* = 3449.7(2) Å³, *Z* = 4, *F*(000) = 1264, *D*_c = 1.134 g cm⁻³, λ = 1.54178 Å, *T* = 90(2) K, μ = 2.978 mm⁻¹, 40970 reflections collected, 6213 unique (*R*_{int} = 0.0908), *R*1 = 0.0761, *wR*2 = 0.2104 (*I* > 2 σ (*I*)). Crystal data for **2**: C₂₉H₅₀BCoN₁₀O_{0.5}, *M* = 616.53, monoclinic, space group *P*2₁/*c*, *a* = 9.9894(2) Å, *b* = 13.7890(3) Å, *c* = 24.3416(6) Å, β = 93.256(1)°, *V* = 3347.5(1) Å³, *Z* = 4, *F*(000) = 1320, *D*_c = 1.223 g cm⁻³, λ = 0.71073 Å, *T* = 90(2) K, μ = 0.549 mm⁻¹, 13593 reflections collected, 7656 unique (*R*_{int} = 0.0464), *R*1 = 0.0607, *wR*2 = 0.1503 (*I* > 2 σ (*I*)). Crystal data for **3**: C₂₉H₅₀BNiN₁₀O_{0.5}, *M* = 616.31, monoclinic, space group *P*2₁/*c*, *a* = 10.0820(1) Å, *b* = 13.7650(2) Å, *c* = 24.3610(6) Å, β = 91.3180(6)°, *V* = 3379.9(1) Å³, *Z* = 4, *F*(000) = 1324, *D*_c = 1.211 g cm⁻³, λ = 0.71073 Å, *T* = 90(2) K, μ = 0.610 mm⁻¹, 15099 reflections collected, 7734 unique (*R*_{int} = 0.0616), *R*1 = 0.0493, *wR*2 = 0.1149 (*I* > 2 σ (*I*)). CCDC 610652 (**1**), 610653 (**2**), 610654 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608297a

- 1 (a) L. M. C. Beltran and J. R. Long, *Acc. Chem. Res.*, 2005, **38**, 325; (b) J. J. Sokol, A. G. Hee and J. R. Long, *J. Am. Chem. Soc.*, 2002, **124**, 7656; (c) C. P. Berlinguette, D. Vaughn, C. Cañada-Vilalta, J. R. Galán-Mascarós and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1523; (d) A. V. Palii, S. M. Ostrovsky, S. I. Klokishner, B. S. Tsukerblat, C. P. Berlinguette, K. R. Dunbar and J. R. Galán-Mascarós, *J. Am. Chem. Soc.*, 2004, **126**, 16860; (e) E. J. Schelter, A. V. Prosvirin, W. M. Reiff and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2004, **43**, 4912; (f) K. R. Dunbar, E. J. Schelter, A. V. Palii, S. M. Ostrovsky, V. Y. Mirovitskii, J. M. Hudson, M. A. Omary, S. I. Klokishner and B. S. Tsukerblat, *J. Phys. Chem. A*, 2003, **107**, 11102; (g) E. J. Schelter, A. V. Prosvirin and K. R. Dunbar, *J. Am. Chem. Soc.*, 2004, **126**, 15004; (h) S. Wang, J.-J. Zuo, H.-C. Zhou, H. J. Choi, Y. Ke, J. R. Long and

- X.-Z. You, *Angew. Chem., Int. Ed.*, 2004, **43**, 5940; (i) M. P. Shores, P. A. Berseth, J. R. Long, V. Marvaud, R. Garde and M. Verdaguer, *Inorg. Synth.*, 2004, **34**, 149; (j) H. Miyasaka, H. Takahashi, T. Madanbashi, K.-I. Sugiura, R. Clérac and H. Nojiri, *Inorg. Chem.*, 2005, **44**, 5969.
- 2 (a) D. Li, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.*, 2006, **45**, 1951; (b) D. Li, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.*, 2006, **45**, 2773; (c) D. Li, S. Parkin, G. Wang, G. T. Yee, R. Clérac, W. Wernsdorfer and S. M. Holmes, *J. Am. Chem. Soc.*, 2006, **128**, 4214; (d) D. Li, R. Clérac, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.*, 2006, **45**, 5251; (e) D. Li, S. Parkin, R. Clérac and S. M. Holmes, *Inorg. Chem.*, 2006, **45**, DOI: 10.1021/ic060695q; (f) D. Li, S. Parkin, G. Wang, G. T. Yee, A. V. Prosvirin and S. M. Holmes, *Inorg. Chem.*, 2005, **44**, 4903; (g) D. Li, S. Parkin, R. Clérac and S. M. Holmes, unpublished results.
- 3 (a) S. Wang, J.-L. Zhu, S. Gao, Y. Song, H.-C. Zhou, Y.-Z. Zhang and X.-Z. You, *J. Am. Chem. Soc.*, 2004, **126**, 8900; (b) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K.-I. Sugiura, M. Yamashita, C. Coulon and R. Clérac, *J. Am. Chem. Soc.*, 2005, **127**, 3090.
- 4 T. Oshiki, K. Mashima, S.-I. Kawamura, K. Tani and K. Kitaura, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1735.
- 5 S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, 1969, **91**, 4181.
- 6 S. Hikichi, Y. Sasakura, M. Yoshizawa, Y. Ohzu, Y. Moro-oka and M. Akita, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 1255.
- 7 K. J. Nelson, I. D. Giles, W. W. Shum, A. M. Arif and J. S. Miller, *Angew. Chem., Int. Ed.*, 2005, **44**, 3129.
- 8 J. P. Eaton and D. Nicholls, *Transition Met. Chem. (Dordrecht, Neth.)*, 1981, **6**, 203.
- 9 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 5th edn, 1997.
- 10 P. A. Berseth, J. J. Sokol, M. P. Shores, J. L. Heinrich and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 9655.
- 11 A. Ludi and H. U. Güdel, *Struct. Bonding (Berlin, Ger.)*, 1973, **14**, 1.
- 12 R. Rupp, G. Huttner, P. Kircher, R. Soltek and M. Buchner, *Eur. J. Inorg. Chem.*, 2000, 1745.
- 13 I. K. Meier, R. M. Pearlstein, D. Ramprasad and G. P. Pez, *Inorg. Chem.*, 1997, **36**, 1707.
- 14 D. A. White, A. J. Solodar and M. M. Baizer, *Inorg. Chem.*, 1972, **11**, 2160.
- 15 J.-F. Bertran, J. B. Pascual and E. R. Ruiz, *Spectrochim. Acta, Part A*, 1990, **46**, 685.
- 16 J. L. Heinrich, P. A. Berseth and J. R. Long, *Chem. Commun.*, 1998, 1231.
- 17 (a) A. Terzis, K. N. Raymond and T. G. Spiro, *Inorg. Chem.*, 1970, **9**, 2415; (b) W. P. Griffith and J. R. Lane, *J. Chem. Soc., Dalton Trans.*, 1972, 158.
- 18 (a) L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 2590; (b) J. J. Sokol, M. P. Shores and J. R. Long, *Angew. Chem., Int. Ed.*, 2001, **40**, 236.
- 19 R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, 1970, **4**, 23.
- 20 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, 1986.
- 21 F. Karadas, E. J. Schelter, A. V. Prosvirin, J. Basca and K. R. Dunbar, *Chem. Commun.*, 2005, 1414.
- 22 (a) F. A. Cotton, L. M. Daniels, T. Lu, C. A. Murillo and X. Wang, *J. Chem. Soc., Dalton Trans.*, 1999, 517; (b) R. Clérac, F. A. Cotton, C. A. Murillo and H.-C. Zhou, *Inorg. Chem.*, 2000, **39**, 3414; (c) R. Clérac, F. A. Cotton, K. R. Dunbar, C. A. Murillo and I. Pascual, *Inorg. Chem.*, 2000, **39**, 748; (d) R. Clérac, F. A. Cotton, K. R. Dunbar, C. A. Murillo and I. Pascual, *Inorg. Chem.*, 2000, **39**, 752.
- 23 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.