

Cite this: *Chem. Commun.*, 2011, **47**, 10007–10009

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COMMUNICATION

Transition metal complexes of the pentacyanocyclopentadienide anion†

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Received 23rd May 2011, Accepted 22nd June 2011

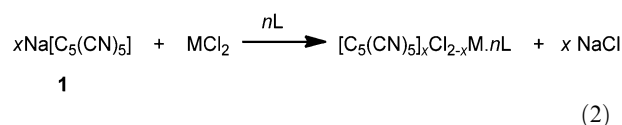
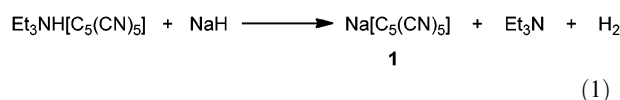
DOI: 10.1039/c1cc13021h

The ready formation of a range of transition metal complexes of the pentacyanocyclopentadienide anion via ligand transfer reactions employing Na[C₅(CN)₅] indicates that the [C₅(CN)₅][−] anion has an extensive transition metal coordination chemistry and is not such a weakly coordinating anion.

The discovery of π -bonding of cyclopentadienide anions in the sandwich structures of transition metal metallocenes, such as ferrocene, cobaltocene and nickelocene, was a landmark in modern chemistry for which Fischer and Wilkinson received the 1973 Nobel Prize.¹ What is less recognised, however, is just how extreme the influence of electron-withdrawing groups can be on the bonding character of the cyclopentadienyl ring. This is most acutely felt in the case of the replacement of the C–H groups of the parent cyclopentadienide anion by C \equiv N groups. For example, even incorporating two C \equiv N groups switches the ligand from the classical π -bonding mode in Cp₂Co to a bridging 1,2-(CN)₂ σ -bonding mode in the polymeric structure of [Co{C₅H₃-1,2-(CN)₂}₄(Me₄N)₂].² This change from Fischer–Wilkinson¹ to Kealy–Pauson³ behaviour makes highly substituted cyclopentadienide ligands of this type of fundamental interest especially in regard to their applications as multi-nodal building blocks in the construction of new magnetic lattices. Most interesting of all in this context is the pentacyanocyclopentadienide anion [C₅(CN)₅][−]⁴ which in theory could function as a planar, five-fold symmetric node, for which there is no matching crystal symmetry.⁵

We showed recently that the chemistry of the pentacyanocyclopentadienide anion can potentially be greatly expanded by the use of ammonium salt [Et₃NH][C₅(CN)₅] which can be employed as a synthon for the Brønsted acid [C₅(CN)₅H].⁶ This approach provides ready access to the sodium salt Na[C₅(CN)₅] (**1**) which is a key starting material in this area (eqn (1)). So far the transition metal coordination chemistry of the [C₅(CN)₅][−] ligand has been almost unexplored possibly because of reports that this ligand is ‘weakly’⁷ or even ‘almost totally non-coordinating’.⁸ Indeed, the only transition metal complex to be structurally characterised so far is the Ag^I complex [Ag{C₅(CN)₅}]_∞ (by powder diffraction).⁵ We report

here the first single-crystal X-ray structures of transition metal compounds containing the [C₅(CN)₅][−] ligand, utilising the metal-exchange reactions of transition metal halides with **1** (eqn (2), where L = a Lewis base donor). This study indicates that the [C₅(CN)₅][−] anion has an extensive transition metal coordination chemistry.



The new compounds [{C₅(CN)₅]₂Co·(H₂O)₂(thf)₂] (**2**) (L = thf), [{C₅(CN)₅]₂CoCl·2thf]_∞ (**3**) (L = thf) and [{C₅(CN)₅]₂Cu·2MeCN]_∞ (**4**) (L = MeCN) were obtained by the reactions of **1** with CoCl₂·*n*H₂O, and anhydrous CoCl₂ and CuCl₂, respectively.† Single crystals of the complexes were obtained by a range of techniques (solvent layering, vapour diffusion and solvent evaporation). In the case of **4** an unexpected reduction occurs from Cu^{II} to Cu^I. This appears to occur slowly during the crystallisation procedure even under nitrogen atmosphere and must, we assume, be associated with an as yet unknown oxidation of the [C₅(CN)₅][−] ligand.

The structure of monomeric **2**† provides an interesting counterpoint to the sandwich-structure of metallocenes such as cobaltocene (Fig. 1).⁹ The complex contains an octahedral Co^{II} centre that is coordinated by two σ -bonded [C₅(CN)₅] ligands as well to two thf and H₂O molecules. This provides a formal electron count of 21e[−] for the Co centre, characteristic of a coordination compound rather than an organometallic. Consistent with this, the Co–N bond lengths in **2** [Co(1)–N(1) 2.1226(16) Å] are as expected for high-spin Co²⁺.¹⁰

The substitution of only one [C₅(CN)₅][−] ligand on to CoCl₂ in the presence of thf as the solvent gives the complex [{C₅(CN)₅]₂CoCl·2thf] (**3**) (Fig. 2). The polymeric structure of **3**† is composed of repeating dimeric Co₂Cl₂ ring units which are linked together by [C₅(CN)₅][−] ligands, using a 1,2-(CN)₂ bridging mode. The result of this bridging is to generate a double-stranded, zig-zagged polymeric chain in which the Co₂Cl₂ rings lie approximately perpendicular to the planes of the [C₅(CN)₅][−] ligands. There are two unique [{C₅(CN)₅]₂CoCl·2thf} monomer units in the unit cell of **3**

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† CCDC 826931–826933. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13021h

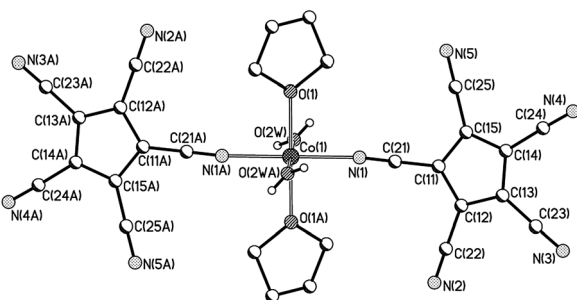


Fig. 1 Monomeric structure of $[\{C_5(CN)_5\}_2Co \cdot (H_2O)_2(thf)_2]$ (**2**). H-atoms (except those on H_2O) and the lattice-bound H_2O and thf ligands have been removed for clarity. Selected bond lengths (Å) and angles ($^\circ$): Co(1)–N(1) 2.1226(16), $C \equiv N$ range 1.136(3)–1.432(2), $C \cdots C(Cp)$ range 1.394(3)–1.412(3), $C-C(\equiv N)$ range 1.419(3)–1.435(3), N(1)–Co(1)–N(1A) 180.0, C(21)–N(1)–Co(1) 165.9(2).

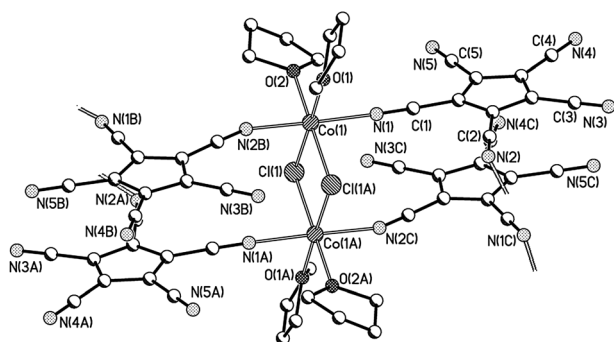


Fig. 2 The structure of **3** illustrated by one of the two independent molecules (H-atoms have been removed). The centrosymmetric chlorine bridged dimeric repeat unit in the polymeric structure of **3**. Selected bond lengths (Å) and angles ($^\circ$) (averaged over both independent molecules): Co–N range 2.12(1)–2.15(1), Co–Cl range 2.371(8)–2.484(9), $C \equiv N$ range 1.136(3)–1.432(2), $C \cdots C(Cp)$ range 1.394(3)–1.412(3), $C-C(\equiv N)$ range 1.419(3)–1.435(3), N–Co–N mean 174.6, Cl–Co–Cl mean 88.2, Co–Cl–Co mean 91.9.

which generate two crystallographically distinct, but chemically similar double-stranded polymers chains running parallel to the c -axis (only one of which is shown in Fig. 2). This structure results in the close approach of the $C_5(CN)_5$ rings which connect the Co_2Cl_2 units in the two strands, with the C_5 rings being almost parallel and separated by mean 3.56 Å. These weak, graphitic-type interactions are also involved in the association of adjacent independent polymer strands in the crystal lattice. The six-coordinate geometry of the Co^{2+} ions of **3** which are bonded axially to two $C \equiv N$ groups (as well as two thf ligands and two Cl^- ions) is similar to that found in the monomer **2**, as are the Co–N bond lengths [range 2.12(1)–2.15(1) Å].

The molecular structure of **4** \ddagger has an unusual helical structure. This contains distorted-tetrahedral Cu^I ions which are coordinated by the two $C \equiv N$ groups of symmetry-related $[C_5(CN)_5]^-$ rings, producing a single-strand polymeric chain running parallel to the c -axis (Fig. 3a). In addition each of the Cu^I ions is also coordinated by two MeCN ligands. The 1,3-bridging mode found in this polymer has been seen previously in the solid-state structure of the dimeric Na

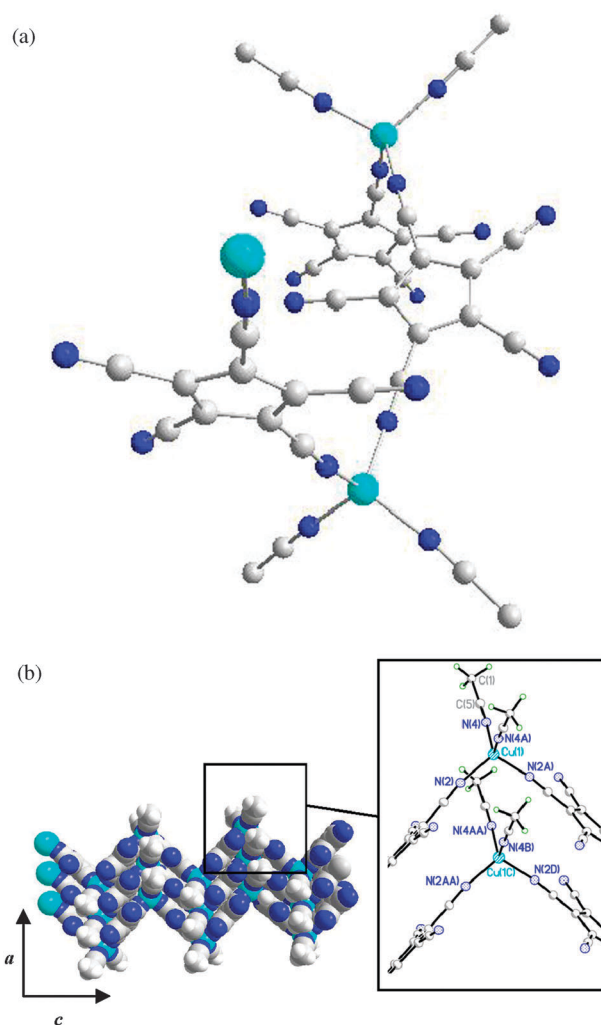


Fig. 3 (a) Part of the left-hand helical strand of **4** generated by the 2_1 -axis (viewed down the c -axis), and (b) the interdigitation of three separate polymer strands viewed onto the crystallographic ac -plane (down the b -axis). Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–N(2) 1.9819(19), Cu(1)–N(4) 1.987(2), Cu(1)– \cdots Cu(1C) 4.903(2), N(2)–Cu(1)–N(2A) 105.85(11), N(4)–Cu(1)–N(4A) 112.14(13).

complex $[(tmeda)_2Na\{C_5(CN)_5\}]_2$.⁶ The bulk sample of **4** is racemic, but adoption of a chiral (orthorhombic $C222_1$) space group in the solid state results in the presence of only one enantiomer in the crystal selected, in this case the left-hand helical polymer. The resolution of enantiomorphs by crystallisation is now fairly common for helical coordination polymers,^{11,12} although these generally occur as co-crystalline, racemic mixtures in centrosymmetric space groups. Examples of homochiral selection of this type are the Cd^{II} complex $[Cd\{5-(9\text{-anthracenyl})pyrimidine\}_2(NO_3)_2 \cdot H_2O \cdot Et_2O]_\infty$ ¹³ and Ag^+ complex $[Ag(pyridazine)_2](BF_4)$.¹⁴

Individual adjacent helical strands of **4** interdigitate *via* their $C_5(CN)_5$ groups, giving an infinite sheet of chains stacked along the a -axis (Fig. 3b). The inter-strand $Cu \cdots Cu$ separation [4.903(2) Å] and $Cu \cdots C(\equiv N)$ [3.937(2) Å] and $Cu \cdots N(\equiv C)$ [3.939(2) Å] contacts between the $(MeCN)_2Cu$ units within the layers of **4** are all well above the values expected even for weak interactions.¹⁵ The layers of helices

in **4** (lying parallel to the *ac* crystal plane) are linked by H-bonding C–H...N≡C interactions between the Me group of the each MeCN ligands and a nitrogen atom [N(2)] of a [C₅(CN)₅][−] ring in the next layer [H...N 2.563(2) Å, *cf* sum of van der Waal's radii of H and N *ca.* 3.0 Å]. The structural arrangement found in **4** is in marked contrast to that found in the unsolvated Ag^I compound [C₅(CN)₅Ag]⁺,⁵ determined by X-ray powder diffraction, which has a polymeric sheet structure containing three-coordinate, trigonal Ag⁺ cations.

In conclusion, the current study shows that the [C₅(CN)₅][−] ligand is likely to have an extensive coordination chemistry with transition metals, provided the appropriate synthetic route is employed. In this context, the previous conclusion that this ligand may have limited applications is in large part the result of the poor ligand-transfer properties of the salt [Et₄N][C₅(CN)₅] used in previous studies⁵ rather than the lack of inherent coordination ability of the donor N atoms.¹⁶ Complexes **2**, **3** and **4** are the first transition metal complexes containing this ligand to be structurally characterised by single-crystal X-ray diffraction. We are continuing our studies in this area, particularly in respect to the applications of the [C₅(CN)₅][−] ligand in magnetic lattices and cages.

We thank The EPSRC (studentship for TCW), The Leverhulme Trust (PDRA for RJL) and Dr J. E. Davies for collecting X-ray data on **2**, **3** and **4**.

Notes and references

† *Synthesis of 2*: a mixture of **1** (50 mg, 0.23 mmol) and CoCl₂·H₂O (28 mg, 0.12 mmol in thf (10 ml) was stirred for 24 h at room temperature. The resulting solution was reduced in volume under vacuum to *ca.* 1 ml and layered with n-hexane at room temperature. Storage for 1 week gave blue crystals of **2** (73 mg, 35%). IR, ν/cm^{-1} = 3560(m), 3478(s) (symm., asym. str. O–H), 2261(s), 2223(s) (C≡N str.), other bands at 1054(w), 1028(s), 918(w), 870(m), 722(m). Calcd. for **2**, C 52.8, H 4.4, N 19.2, found, C 50.0, H 3.9, N 18.6.

Synthesis of 3: **1** (5mg, 2.35×10^{-5} mols) was stirred for 18 h with oven dried cobalt (ii) chloride (4mg, 3.08×10^{-5} mols) in thf (10 ml) at room temperature. The solution was reduced to 1ml *in vacuo* and red crystals of **3**·0.25thf were grown by vapour diffusion using n-pentane as the non-solvent in *ca.* 5 days at room temperature. Yield 5 mg (24%). IR, ν/cm^{-1} = 2266(s) (C≡N str.), other bands at 1306(s), 1262(s), 1155(m), 1098 (m), 722(s). Elemental analysis, found for C 44.6, H 1.98, N 21.1, calcd. for **3**·3.25thf, C 45.0, H 1.3, N 21.8.

Synthesis of 4: **1** (5 mg, 2.35×10^{-5} mols) was stirred for 18 h with oven dried copper (ii) chloride (4 mg, 2.97×10^{-5} mols) in acetonitrile (10 ml) at room temperature. The solution was reduced to 1ml *in vacuo* and crystallised by vapour diffusion using diethyl ether as the non-solvent. Initially brown crystals of an unidentified complex grew (repeated attempts to obtain a single crystal of this species for X-ray analysis failed). The reaction was left slightly open to air to let the solvent evaporate slowly off, and a yellow/brown, crystalline material formed. Yield 7 mg (82%). IR, ν/cm^{-1} = 2222 (vs) (C≡N str.), other bands at 1651(br.s), 1583(m), 1478(m) 1470(vs), 1365(m), 1033 (br.m), 874(br.m). ¹H NMR (500.05 MHz, + 25 °C, d₆-dmsO),

δ (ppm) = 2.07. ¹³C{¹H} NMR (125.7 MHz, + 25 °C, d₆-dmsO), δ (ppm) = 118.0 (MeCN, C≡N) 113.2 (C₅(CN)₅, C≡N), 101.9 (C₅(CN)₅, ring C), 1.3 (MeCN, Me). Satisfactory elemental analysis could not be obtained because samples of **4** were contaminated with the NaCl byproduct from the reaction.

Crystal data for 2·H₂O; C₃₂H₃₂CoN₁₀O₇, *M* = 727.61, triclinic, space group *P* $\bar{1}$, *Z* = 1, *a* = 8.4871(3), *b* = 10.6177(4), *c* = 10.7684(4) Å, α = 107.933(2), β = 98.454(2), γ = 101.237(2)°, *V* = 882.97(6) Å³, μ (Mo–K α) = 0.546 mm^{−1}, ρ_c = 1.368 Mg m^{−3}, *T* = 180(2)K. Total reflections 8990, unique 3784 (*R*_{int} = 0.038). *R*₁ = 0.039 [*I* > 2 σ (*i*)] and *wR*₂ = 0.104 (all data).

Crystal data for 3·0.25thf; C₃₈H₃₆Cl₂Co₂N₁₀O_{4.25}, *M* = 889.53, monoclinic, space group *P*2/*c*, *Z* = 4, *a* = 14.803(3), *b* = 19.960(4), *c* = 14.727(3) Å, β = 103.18(3)°, *V* = 4236.6(15) Å³, μ (Mo–K α) = 0.960 mm^{−1}, ρ_c = 0.960 Mg m^{−3}, *T* = 180(2)K. Total reflections 34919, unique 7390 (*R*_{int} = 0.050). *R*₁ = 0.075 [*I* > 2 σ (*i*)] and *wR*₂ = 0.224 (all data).

Crystal data for 4; C₁₄H₆CuN₇, *M* = 335.80, orthorhombic, space group *C*222₁(1), *Z* = 4, *a* = 4.80260(10), *b* = 20.3040(5), *c* = 15.9930(5) Å, *V* = 1559.51(7) Å³, μ (Mo–K α) = 1.441 mm^{−1}, ρ_c = 1.976 Mg m^{−3}, *T* = 180(2)K. Total reflections 7371, unique 2613 (*R*_{int} = 0.032). *R*₁ = 0.031 [*I* > 2 σ (*i*)] and *wR*₂ = 0.108 (all data).

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