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Use of dipotassium cyanamide for the synthesis of cyanoimido (NCN^{2-}) complexes of tungsten and cobalt

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Three transition metal cyanoimido (NCN^{2-}) complexes, $(Cp^*WS_2)_2(\mu\text{-}NCN)$ (1) ($Cp^* = \eta^5\text{-}C_5Me_5$), $K[(Cp^*WS_2)_2(NCN)]$ (2) and $\{[(bipy)_2Co]_2(\mu\text{-}NCN)_2\}(ClO_4)_2$ (3), were synthesized from dipotassium cyanamide, and their structures were determined.

Cyanamide ($NCNH_2$) and its basic forms ($NCNH^-$ and NCN^{2-}) have been known for many years, and the recognition that cyanamide can be a substrate of nitrogenases and cyanamide hydratase[1] has renewed attention by chemists.[2] Although the preparation of the alkali and alkaline earth metal salts of cyanamide is established,[2–7] their use in transition metal coordination chemistry has not been well investigated. The structures of NCN^{2-} reported so far are mostly the organic and main-group metal derivatives, *e.g.*, $(CH_3)_3MNCNM(CH_3)_3$ (M = Si, Ge, Sn).[8–10] Although several cyanoimido complexes of transition metals have been reported,[2,11–14] the NCN^{2-} group derives from cyanamide ($NCNH_2$) and diorganocyanamides such as 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene[12,13], or from cyanation of nitrido (N^{3-}) complexes,[14] where redox reactions of transition metals are involved.[2,13] In this communication, we report the synthesis and structures of the three new cyanoimido complexes, $(Cp^*WS_2)_2(\mu\text{-}NCN)$ (**1**), $K[(Cp^*WS_2)(NCN)]$ (**2**) and $\{[(bipy)_2Co]_2(\mu\text{-}NCN)_2\}(ClO_4)_2\cdot CH_3CN$ (**3**·CH_3CN), which were prepared directly from transmetallation reactions of dipotassium cyanamide, $K_2(NCN)$.

The reaction between Cp^*WS_2Cl and 1/2 equiv. of $K_2(NCN)$ in THF–MeOH gave rise to the dinuclear complex **1** as black crystalline plates in 67.3% yield.† According to the X-ray crystal analysis,‡ complex **1** consists of two Cp^*WS_2 units bridged by an $[NCN]^{2-}$ ligand (Fig. 1), and a crystallographically imposed inversion center resides at the cyanoimide carbon. The tungsten atom adopts a distorted tetrahedral geometry with typical W=S bond distances (av. 2.155 Å). The linear end-on coordination of $[NCN]^{2-}$ at W (WNC = 176.4(4)°) appears to illustrate possible electron donation from the NCN occupied π orbitals to vacant W d_π orbitals. However, the W–N distance of 1.942(5) Å is longer, and the N–C distance of 1.197(5) Å is shorter than the corresponding Mo–N (1.852(7) Å) and N–C (1.233(7) Å) bond lengths in $\{Mo[N(Pr^i)Ar]_3\}_2(\mu\text{-}NCN)$.[13] Therefore, the W–NCN π interactions are not expected to be large, probably because the terminal sulfide (S^{2-}) is a stronger π donor than $[NCN]^{2-}$. The cyclic voltammogram of **1** in CH_2Cl_2 shows two quasi-reversible redox couples at $E_{1/2} = -1.106$ V and $E_{1/2} = -1.490$ V, which may be ascribed to the two reductive processes of W(VI)–NCN–W(VI) ↔ W(V)–NCN–W(VI) ↔ W(V)–NCN–W(V). Appearance of the two well-defined redox couples indicates that the two W centers communicate electronically through the NCN bridge.

When the reaction of Cp^*WS_2Cl was carried out with 1 equiv. of $K_2(NCN)$, red crystals of the mononuclear complex **2** were isolated in 25.0% yield. Crystals of **2** contain $[Cp^*WS_2(NCN)]^-$ anions and K^+ cations, and each K^+ cation has short contacts with two terminal N atoms (K–N 2.732(4), 2.800(6) Å). Thus two $[Cp^*WS_2(NCN)]^-$ complex anions may be considered to be weakly linked by two K^+ cations. The distances between K^+ and the neighbouring S atoms are long, 3.19–3.45 Å. Although the coordination geometry at W resembles that of **1**, there are some interesting differences in the bond distances (Fig. 2). The W–N distance is 0.08 Å shorter for **2** (1.858(4) Å), and the average W–S distance (2.197 Å) is 0.04 Å longer. This observation points to a stronger W–N π bonding for **2**, whereas the coordination of NCN^{2-} occurs with the slightly bent WN(1)C angle of 154.8(3)°. The two N–C distances in NCN^{2-} are notably different due to a contribution from the $N{\equiv}C\text{–}N^{2-}$ resonance form, as was observed for $Mo(NCN)_2(dppe)_2$[2] and $(Et_4N)[Os(bpy)(Cl)_3(NCN)]$.[14] The successful isolation of **2** reveals that formation of **1** by the transmetallation reaction of $K_2(NCN)$ with Cp^*WS_2Cl takes place in a stepwise manner, and indicates a possibility of introducing two different metal complexes at the two ends of NCN^{2-}.

Next, we examined the reaction of $K_2(NCN)$ with an electron rich Co(II) complex. Thus $Co(ClO_4)_2.6H_2O$ was treated with 1/2 equiv. of $K_2(NCN)$ in CH_3CN in the presence of 4 equiv. of 2,2′-bipyridine (bipy), from which we isolated $\{[(bipy)_2Co]_2(\mu\text{-}NCN)_2\}(ClO_4)_2$ (**3**) as black crystals in 25.4% yield. The X-ray analysis shows an unusual dinuclear structure where the two Co

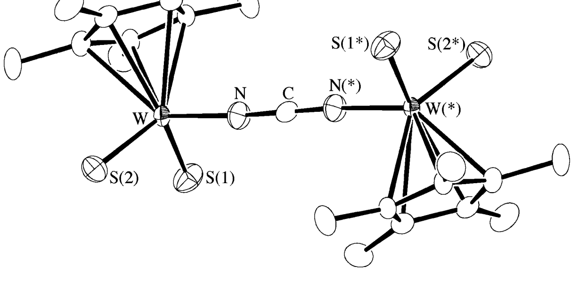

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): W–S(1) 2.151(1), W–S(2) 2.160(1), W–N 1.942(5), N–C 1.197(5), S(1)–W–S(2) 106.20(8), S(1)–W–N 102.42(18), S(2)–W–N 103.35(19), W–N–C 176.4(4).

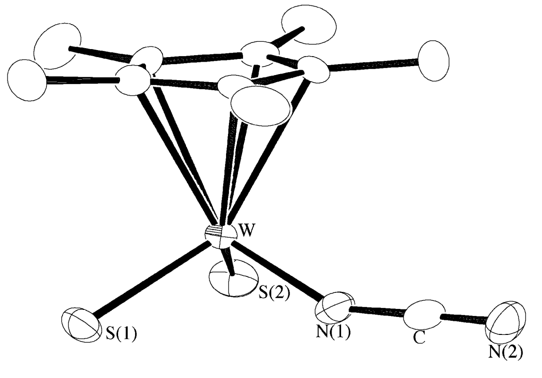

Fig. 2 Complex anion of **2**. Selected bond lengths (Å) and angles (°): W–S(1) 2.191(1), W–S(2) 2.203(1), W–N(1) 1.858(4), N(1)–C 1.268(6), N(2)–C 1.174(6), S(1)–W–S(2) 104.66(5), S(1)–W–N(1) 102.95(13), S(2)–W–N(1) 103.42(13), W–N(1)–C 154.8(3), N(1)–C–N(2) 178.5(5).

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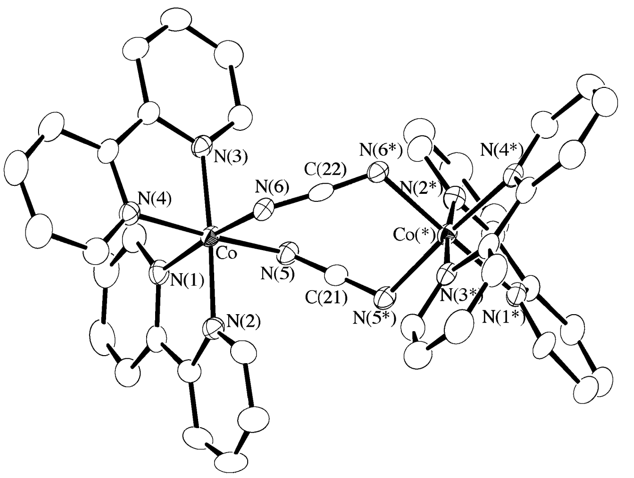

Fig. 3 Complex cation of **3**. Selected bond distances (Å) and angles (°): Co–N(1) 1.978(4), Co–N(2) 1.941(4), Co–N(3) 1.934(4), Co–N(4) 1.976(4), Co–N(5) 1.942(4), Co–N(6) 1.954(4), N(5)–C(21) 1.226(4), N(6)–C(22) 1.229(4), Co–N(5)–C(21) 115.9(3), Co–N(6)–C(22) 118.6(3), N(5)–C(21)–N(5*) 178.1(6), N(6)–C(22)–N(6*) 175.7(6).

atoms are bridged by two $[NCN]^{2-}$ ligands, and a crystallographic C_2 axis runs through the two cyanoimide carbon atoms (Fig. 3). During this reaction, the cobalt was oxidized from Co(II) to Co(III), presumably by oxygen in the air or by perchlorate. Each Co is further coordinated by two bipy chelates, forming a stable octahedral coodination geometry with six nitrogen atoms. The Co–N_{bipy} bond lengths are normal with the average value of 1.957 Å. The average Co–$N_{cyanoimide}$ distance of 1.948 Å is nearly the same as that of **1**, despite the fact that the ionic radii of Co(III) is 0.055 Å smaller.[15] The long Co–$N_{cyanoimide}$ bonds and the concomitant small CoNC angles of 117.6° (av.) are consistent with the anticipation that there is no π bonding between the electron rich Co atoms and NCN^{2-}. On the other hand, the average N–C distance in $[NCN]^{2-}$ (1.228 Å) is somewhat longer than that in **1** (1.197(5) Å).

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Notes and references

† Complexes **1** and **2** were prepared under argon using Schlenk techniques and dry solvents. $(Cp^*WS_2)_2(\mu\text{-NCN})$ (**1**): $NCNH_2$ (10.5 mg, 0.25 mmol) was reacted with ${}^tBuOK$ (56.1 mg, 0.5 mmol) in methanol (10 ml) at 0 °C for 2 h to give a clear solution, to which a slurry of Cp^*WS_2Cl (209.3 mg, 0.5 mmol) in THF (20 ml) was added. After stirring for 38 h at room temperature, the solvent was dried and the brown residue was extracted by toluene (6 ml). Layering hexane on the resulting brown solution gave rise to black crystalline plates of **1** (135.7 mg, 67.3%). Found: C, 31.38; H, 3.84; N, 3.46. $C_{21}H_{30}N_2S_4W_2$ requires C, 31.28; H, 3.75; N, 3.47%. ${}^1H$ NMR (500 MHz $CDCl_3$): δ 2.29 (s, Cp*). IR (cm^{-1}, KBr): 2087vs (NCN), 475s (W=S).

$[(Cp^*WS_2)(NCN)]K$ (**2**): a mixture of $NCNH_2$ (21 mg, 0.50 mmol) and ${}^tBuOK$ (112.2 mg, 1.0 mmol) in methanol (10 ml) was stirred at 0 °C for 2 h, to which a slurry of Cp^*WS_2Cl (209.3 mg, 0.5 mmol) in THF (20 ml) was slowly added over 3 h. After stirring the reaction mixture for 12 h at room temperature, the solvent was removed and the brown residue was extracted by THF (6 ml). Layering ether on the resulting red solution yielded red crystals of **2** (58.0 mg, 25.0%). Found: C, 28.38; H, 3.40; N, 5.90. $C_{11}H_{15}N_2S_2KW$ requires C, 28.58; H, 3.27; N, 6.06%. ${}^1H$ NMR (500 MHz CD_3CN): δ 2.11 (s, Cp*). IR (cm^{-1}, KBr): 2083vs (NCN), 461s (W=S).

$\{[(bipy)_2Co]_2(\mu\text{-NCN})_2\}(ClO_4)_2\cdot CH_3CN$ (**3**·CH_3CN): $NCNH_2$ (10.5 mg, 0.25 mmol) was treated with ${}^tBuOK$ (56.1 mg, 0.5 mmol) in methanol (10 ml) at 0 °C for 2 h, and the resulting clear solution was added to a mixture of $Co(ClO_4)_2\cdot 6H_2O$ (183.0 mg, 0.5 mmol) (*warning: possible explosion may occur and the experiment must be run on a small scale*) and 2,2′-bipyridine (156.2 mg, 1 mmol) in CH_3CN (30 ml) in air. After stirring it for 24 h, the solution was filtered and stood in air for several days to yield black crystals of **3** (33.7 mg, 25.4% based on $NCNH_2$). Found: C, 48.89; H, 3.48; N, 17.16. $C_{44}H_{35}N_{13}Cl_2O_8Co_2$ requires C, 49.73; H, 3.32; N, 17.14%. ${}^1H$ NMR (500 MHz, DMSO-d_6): δ 7.34–9.06 (m, bipy). IR (KBr, cm^{-1}): 1943s (NCN).

‡ Crystal data for **1**: $C_{21}H_{30}N_2S_4W_2$, M = 806.427, triclinic, space group $P1$, a = 7.7039(7), b = 12.267(1), c = 7.3201(5) Å, α = 99.980(2), β = 111.0132(1), γ = 96.228(4)°, V = 624.93(9) Å^3, Z = 1, T = 193 K, μ(Mo-Kα) = 95.5 cm^{-1}. The refinement of 133 variables resulted in $R(wR)$ = 0.043(0.115) based on the $F_o{}^2$ data set of 2610 reflections ($I \geq 2.0\ \sigma(I)$).

For **2**: $C_{11}H_{15}N_2S_2WK$, M = 462.32, monoclinic, space group $P2_1/c$, a = 12.215(1), b = 9.364(1), c = 12.9428(3) Å, β = 96.4420(6)°, V = 1471.1(2) Å^3, Z = 4, T = 193 K, μ(Mo-Kα) = 83.99 cm^{-1}. The refinement of 154 variables converged at $R(wR)$ = 0.033(0.086) based on the $F_o{}^2$ data set of 3216 reflections ($I \geq 2.0\ \sigma(I)$).

For **3**·CH_3CN: $C_{44}H_{35}N_{13}Cl_2O_8Co_2$, M = 1062.61, monoclinic, space group $C2/c$, a = 24.096(2), b = 15.189(4), c = 13.9472(4) Å, β = 110.9349(7)°, V = 4767.5(8) Å^3, Z = 4, T = 193 K, μ(Mo-Kα) = 8.74 cm^{-1}. The refinement of 307 variables converged at $R(wR)$ = 0.085(0.207) based on the $F_o{}^2$ data set of 5398 reflections ($I \geq 2.0\ \sigma(I)$). The CH_3CN solvent molecule in the crystal was disordered and the coordinates and occupancy were fixed in the refinement.

CCDC 183859–183861. See http://www.rsc.org/suppdata/cc/b2/b203411e/ for crystallographic data in CIF or other electronic format.

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