The preparation and characterization of square-planar tetrakis(cyanoacetylide) complexes: $[M^{II}(C{\equiv}C{-}C{\equiv}N)_4]^{2-}$ (M = Ni, Pd, Pt)

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Complexes $[M^{II}(C{\equiv}C{-}C{\equiv}N)_4]^{2-}$ (M = Ni, Pd, Pt) are prepared for the first time and the structure of $[NEt_4]_2[Ni(C{\equiv}C{-}C{\equiv}N)_4]$ is determined to have a square-planar geometry.

The cyanide ligand can bridge between two metal ions by bonding to both the C and N and several classes of materials with both extended bonding and interesting solid-state properties exist. These include (*a*) metal-like as well as luminescent one-dimensional (linear chain) materials based on tetracyanoplatinum(II), $[Pt^{II}(CN)_4]^{2-}$,[1] (*b*) two-dimensional (layered) network solids based on the Hofmann clathrates,[2] and (*c*) three-dimensional network solids based on hexacyanometallates, *e.g.* Prussian blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}xH_2O$.[3] Similar structures and electronic properties with enhanced separations between metal sites are expected with the cyanoacetylide, $-C{\equiv}C{-}C{\equiv}N$, L^-, ligand.

The coordination chemistry of L is not well developed. The Pt^{II} complex *cis*-$[Pt(C{\equiv}N)(C{\equiv}C{-}C{\equiv}N)(PPh_3)_2]$[4] was characterized by X-ray diffraction to possess a linear Pt-L^- fragment. This complex was prepared from the oxidative addition of dicyanoacetylene. L was also used to make $[Fe^{II}(CO)_2(C_5H_5)(C{\equiv}C{-}C{\equiv}N)]$ which was subsequently utilized to prepare $[\mu\text{-}\eta^2\text{-}Fe(C{\equiv}C{-}C{\equiv}N)(C_5H_5)(CO)_2][Co(CO)_3]_2$ which possesses the $FeC{\equiv}C{-}C{\equiv}N$ moiety with the $C{\equiv}C$ group π-bound to the binuclear $[Co(CO)_3]_2$ fragment.[5] HC_3N can also serve as a four-electron alkyl donor.[6] Also $[Co(C{\equiv}C{-}C{\equiv}N)_2(C_5H_5)(PPh_3)]$[7] has been prepared and it is the only complex with more than one L ligand reported to date. Herein we report the preparation of $[M(C{\equiv}C{-}C{\equiv}N)_4]^{2-}$ (M = Ni, Pd, Pt).

$[NEt_4]_2[Ni(C{\equiv}C{-}C{\equiv}N)_4]$ was prepared from the reaction of $[NEt_4]_2[NiCl_4]$ and $Me_3SnC{\equiv}C{-}C{\equiv}N$[8] in *N,N*-dimethylformamide.† $[NEt_4]_2[Ni(C{\equiv}C{-}C{\equiv}N)_4]$ has the expected square-planar structure‡ with average Ni–C, C≡C, C–C and C≡N distances of 1.856, 1.203, 1.373 and 1.148 Å, respectively, while the average C–Ni–C, Ni–C–C, C–C–C and C–C–N angles are 90.5, 178.1, 177.0 and 178.8°, respectively, Fig. 1. The Ni–C distance of 1.856 Å is consistent with Ni–C distance in $[Ni(CN)_4]^{2-}$[8] (1.86 Å) and *trans*-$[Ni(PEt_3)_2(CCPh)_2]$ (1.87 Å).[10] The observed IR and ^{13}C NMR as well as electronic absorption spectral data are presented in Table 1.

Metal-to-ligand backbonding is evident from the ν(C≡C) absorptions which are reduced from 2060 cm^{-1} in HC_3N and 2062 cm^{-1} in $K_2[Ni(C_2Ph)_4]^{2-}$[11] to 2039 to 2047 cm^{-1} in

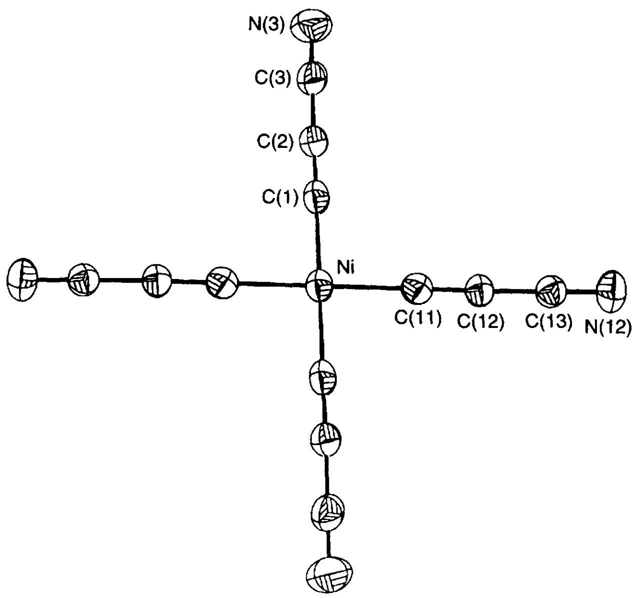

Fig. 1 ORTEP atom-labelling illustration of the $[Ni(C_3N)_4]^{2-}$ ion

Table 1 Physical properties of $[M(C{\equiv}C{-}C{\equiv}N)_4]^{2-}$ (M = Ni, Pd, Pt)

		Metal		
		Ni	Pd	Pt
IR	ν(C≡N)/cm^{-1} [a]	2208s, 2170m	2217s, 2180m	2214s
	ν(C≡C)/cm^{-1} [a]	2039s	2049s	2047m
	ν(M–C)/cm^{-1} [a]	523m	519m	519m
	δ(M–C≡C)/cm^{-1} [a]	427m	409m	413w
NMR	δ(*C*CCN)[b]	107.0	107.1	115.3 (J_{Pt-C} 1034.5 Hz)
	δ(C*C*CN)[b]	80.0	76.1	74.5 (J_{Pt-C} 311.2 Hz)
	δ(CC*C*N)[b]	126.6	122.1	107.8 (J_{Pt-C} 35.9 Hz)
UV-VIS	$\tilde{\nu}_{max}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})	29 410 (27 750)	36 500 (16 320)	30 490 (9 135)
		32 050 (6 560)	38 460 (21 600)	32 050 (16 360)
		39 060 (6 565)	43 100 (19 500)	34 480 (8 525)
		43 780 (21 040)		36 230 (16 445)
				38 460 (11 345)
				42 375 (22 200)
				43 480 (21 600)
	mp[c]/°C	129–132	141–143	204–206

[a] As Nujol mull. [b] In CD_3CN at room temperature. [c] With decomposition.

$[M(C_3N)_4]^{2-}$ (M = Ni, Pd, Pt). The 1.205 Å average C≡C bond distance for $[Ni(C_3N)_4]^{2-}$ is slighter longer than the 1.18 Å value reported for HCCCN[12] while the average CC–CN and C≡N bond distances are 1.373 and 1.148 Å, respectively, which are consistent with 1.38 and 1.14 Å values reported for HCCCN.[12] Hence a small contribution of the M=C=C=C=N, as suggested for *cis*-$[Pt(C{\equiv}N)(C{\equiv}C{-}C{\equiv}N)(PPh_3)_2]$,[4] is evident. Consistent with the major contribution being M–C≡C–C≡N, the ν(C≡N) absorptions are shifted to higher frequency by 69 ± 5 cm^{-1} for $[Ni(C_3N)_4]^{2-}$ with the 2135, 2143 and 2150 cm^{-1} values reported for $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt), respectively.[13] The availability of $[M(C_3N)_4]^{2-}$, albeit with some instability in solution, now afford the possibility to prepare one, two, and three-dimensional solids with unusual electrical, optical and magnetic properties.

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Footnotes

† In a typical experiment Et_3SnC_3N (0.665 g, 2.60 mmol) was dissolved in 13 ml of dmf in a Schlenk flask under nitrogen. After cooling in an ice bath, $[NEt_4]_2[NiCl_4]$ (0.150 g, 0.325 mmol) was added, with stirring for 20 min. Then the cold bath was removed and the pale yellow solution was stirred at room temp. under nitrogen overnight and the colour turned to brown–yellow. The solution was then added to 100 ml of dry, N_2-saturated diethyl ether *via* a cannula with stirring. The resulting yellow precipitate was collected by filtration and dried *in vacuo* (0.134 g, 0.258 mmol, 79%). Purification was effected by filtration of a CH_2Cl_2 solution and removal of CH_2Cl_2 from filtrate gave a pure sample. The formed complex was stable in air in the solid state, however, it is not stable in solution even under nitrogen at low temperature and it partially decomposed to a black polymer. Crystals of $[NEt_4]_2[Ni(C_3N)_4]$ were grown by vapour diffusion of diethyl ether into a Schlenk flask containing 15 mg of product dissolved in 1.5 ml of dmf. $[NEt_4]_2[PdCl_4]$ was used to prepare $[NEt_4]_2[Pd(C_3N)_4]$, while $[NEt_4]_2[PtCl_4]$ with 10 mg of $PdCl_2(NCMe)_2$ catalyst was used to prepare $[NEt_4]_2[Pt(C_3N)_4]$ (without the catalyst the reaction takes several days). Elemental analysis: calc. (found) for $C_{28}H_{40}N_6Ni$: C, 64.75 (64.78); H, 7.76 (7.70); N, 16.18 (16.94%). $C_{28}H_{40}N_6Pd$: C, 59.31 (59.03); H, 7.11 (7.04); N, 14.82 (14.76%). $C_{28}H_{40}N_6Pt$: C, 51.29 (51.09); H, 6.15 (6.16); N, 12.82 (12.71%).

‡ *Crystal data* for $C_{28}H_{40}N_6Ni$, M = 519.38, monoclinic, space group $P2_1/n$, a = 7.484 (2), b = 11.889 (3), c = 17.226 (4) Å, β = 94.78 (2)°, U = 1527.5 Å^3, $F(000)$ = 556, Z = 2, D_c = 1.229 g cm^{-3}, λ = 0.71073 Å, crystal size 0.28 × 0.25 × 0.23 mm, T = 18 °C, $2\theta_{max}$ = 48°, wR (on F) [R (on F)] = 0.0404 (0.0372), for 1531 unique reflections with $I > 3\sigma(I)$. Data was collected on a Syntex $P\bar{1}$ diffractometer and the crystal structure solved using Molen software distributed by Enraf Nonius. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/151.

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