Dicyanogen Trapped in a Solid Matrix at Room Temperature: X-ray Structure of *trans*-[Ni(CN)$_2$(PPh$_3$)$_2$]·(C$_2$N$_2$)

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In the course of our studies on the activation of C$_2$N$_2$ by metal centres in homogeneous phase [1] we took into account the potential reactivity of [Ni(CO)$_2$(PPh$_3$)$_2$] (*1*) with C$_2$N$_2$ at ambient conditions in aprotic solvents.

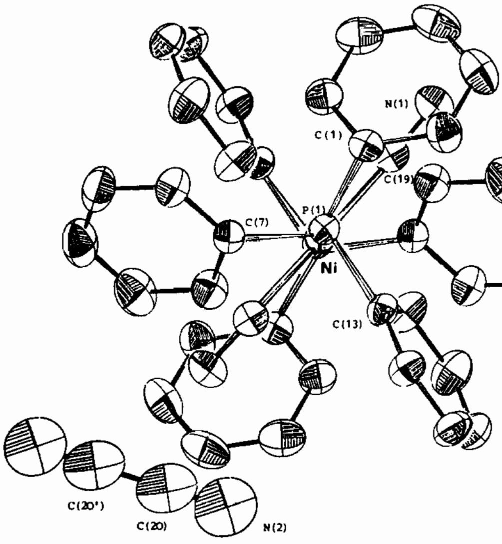

Fig. 1. ORTEP view of the structure of (*2*).

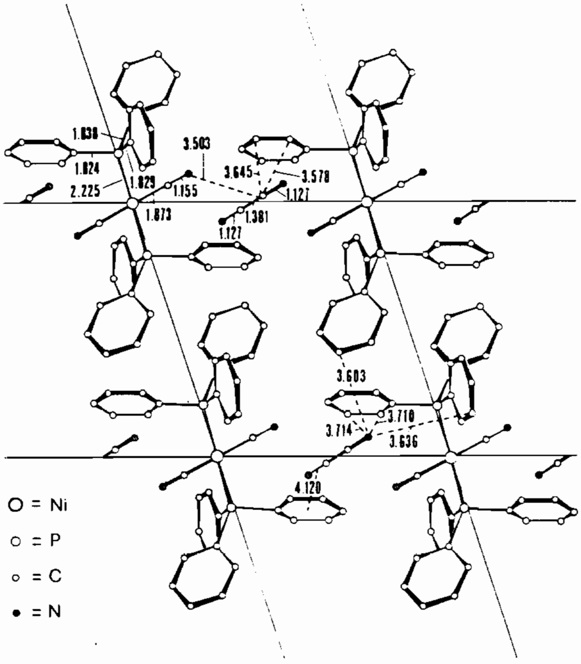

Fig. 2. View of the cell of (*2*) along the 001 direction.

(*1*) is found to react quantitatively with C$_2$N$_2$ in dichloromethane and toluene with complete release of CO and formation of a yellow compound exhibiting a medium-strong, very sharp single band at 2120 cm^{-1} attributable to two mutually *trans* CN ligands bound to nickel(II) in a square planar configuration [2]. The elemental analysis of this complex was found to correspond to the composition [Ni(CN)$_2$(PPh$_3$)$_2$]·(C$_2$N$_2$) (*2*) or to [Ni(CN)$_2$(PPh$_3$)$_2$]·(CH$_2$Cl$_2$)$_x$ (*3*) (x = 0.5÷1.5) when toluene or dichloromethane was used as a solvent. No i.r. evidence of any incorporation of C$_2$N$_2$ was obtained, but mass spectrometry, thermogravimetric analysis (TG) and gas-chromatography gave unambiguous proof of the presence in the crystals (*2*) of one molecule of C$_2$N$_2$ per mol of [Ni(CN)$_2$(PPh$_3$)$_2$].

TABLE I. Selected Interatomic and Intermolecular Distances (Å) and Angles (°) for *trans*-[Ni(CN)$_2$(PPh$_3$)$_2$]·(C$_2$N$_2$).

Ni–P	2.225(0.001)	C(19)–Ni–P	92.5(0.1)
Ni–C(19)	1.873(0.003)	C(19)–Ni–P′	87.4(0.1)
C(19)–N(1)	1.155(0.004)	C(7)–P–C(13)	108.9(0.2)
P–C(1)	1.838(0.004)	Ni–C(19)–N(1)	178.4(0.3)
P–C(7)	1.824(0.003)	Ni–P–C(1)	121.2(0.2)
P–C(13)	1.829(0.003)	Ni–P–C(7)	111.4(0.3)
C(20)–C(20′)	1.381(0.008)	Ni–P–C(13)	108.9(0.2)
C(20)–N(2)	1.127(0.008)	C(20′)–C(20)–N(2)	179.7(0.7)

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TABLE II. Atomic Fractional Coordinates and Thermal Parameters for $[Ni(CN)_2(PPh_3)_2]\cdot(C_2N_2)$.

Atom	X/A	Y/B	Z/C	K	U11	U22	U33	U23	U13	U12
Ni	0.0	0.0	0.0	0.5000	0.0231	0.0312	0.0270	0.0036	0.0118	0.0118
	0.0	0.0	0.0	0.0	0.0002	0.0003	0.0003	0.0002	0.0002	0.0002
P1	0.2024	0.0102	0.0140	1.0000	0.0239	0.0308	0.0295	0.0106	0.0121	0.0126
	0.0001	0.0001	0.0001	0.0	0.0003	0.0003	0.0004	0.0003	0.0003	0.0003
N1	0.1162	0.2919	0.2760	1.0000	0.0454	0.0433	0.0435	0.0039	0.0130	0.0160
	0.0003	0.0003	0.0003	0.0	0.0014	0.0014	0.0014	0.0012	0.0011	0.0011
N2	0.0761	0.6685	0.4419	1.0000	0.0911	0.1283	0.1017	0.0389	0.0424	0.0538
	0.0005	0.0006	0.0006	0.0	0.0031	0.0040	0.0034	0.0030	0.0027	0.0029
C1	0.3550	0.1379	0.1896	1.0000	0.0212	0.0385	0.0328	0.0079	0.0129	0.0139
	0.0002	0.0003	0.0003	0.0	0.0012	0.0013	0.0013	0.0011	0.0010	0.0010
C2	0.4352	0.0825	0.2880	1.0000	0.0383	0.0462	0.0393	0.0137	0.0115	0.0189
	0.0003	0.0004	0.0003	0.0	0.0015	0.0016	0.0016	0.0013	0.0012	0.0013
C3	0.5546	0.1842	0.4146	1.0000	0.0365	0.0707	0.0430	0.0142	0.0070	0.0228
	0.0003	0.0004	0.0004	0.0	0.0016	0.0022	0.0017	0.0016	0.0013	0.0016
C4	0.5937	0.3401	0.4426	1.0000	0.0321	0.0619	0.0134	−0.0055	0.0087	0.0081
	0.0003	0.0004	0.0004	0.0	0.0016	0.0021	0.0017	0.0015	0.0013	0.0015
C5	0.5135	0.3962	0.3444	1.0000	0.0171	0.0393	0.0635	−0.0002	0.0174	0.0059
	0.0003	0.0004	0.0004	0.0	0.0019	0.0017	0.0022	0.0015	0.0016	0.0014
C6	0.3947	0.2961	0.2192	1.0000	0.0388	0.0401	0.0517	0.0110	0.0123	0.0151
	0.0003	0.0003	0.0004	0.0	0.0016	0.0015	0.0018	0.0014	0.0014	0.0013
C7	0.2098	−0.1790	−0.0045	1.0000	0.0248	0.0321	0.0349	0.0105	0.0091	0.0118
	0.0002	0.0003	0.0003	0.0	0.0012	0.0013	0.0013	0.0011	0.0010	0.0010
C8	0.1674	−0.2602	0.0958	1.0000	0.0415	0.0133	0.0495	0.0208	0.0216	0.0181
	0.0003	0.0003	0.0004	0.0	0.0017	0.0016	0.0018	0.0014	0.0014	0.0013
C9	0.1698	−0.4050	0.0883	1.0000	0.0530	0.0438	0.0645	0.0281	0.0141	0.0150
	0.0003	0.0004	0.0004	0.0	0.0019	0.0017	0.0021	0.0016	0.0016	0.0015
C10	0.2125	−0.4699	−0.0218	1.0000	0.0586	0.0399	0.0729	0.0163	0.0083	0.0260
	0.0004	0.0004	0.0005	0.0	0.0021	0.0018	0.0024	0.0017	0.0018	0.0016
C11	0.2545	−0.3902	−0.1214	1.0000	0.0631	0.0529	0.0705	0.0096	0.0272	0.0758
	0.0004	0.0004	0.0005	0.0	0.0021	0.0019	0.0023	0.0017	0.0018	0.0017
C12	0.2543	−0.2447	−0.1133	1.0000	0.0452	0.0136	0.0175	0.0143	0.0225	0.0232
	0.0003	0.0003	0.0004	0.0	0.0016	0.0016	0.0017	0.0013	0.0014	0.0013
C13	0.2389	0.0796	−0.1486	1.0000	0.0330	0.0324	0.0339	0.0134	0.0179	0.0145
	0.0003	0.0003	0.0003	0.0	0.0013	0.0012	0.0013	0.0010	0.0011	0.0010
C14	0.3679	0.1255	−0.1519	1.0000	0.0358	0.0617	0.0514	0.0313	0.0221	0.0248
	0.0003	0.0004	0.0004	0.0	0.0015	0.0019	0.0012	0.0015	0.0014	0.0014
C15	0.3934	0.1802	−0.2747	1.0000	0.0172	0.0635	0.0618	0.0335	0.0366	0.0226
	0.0003	0.0004	0.0004	0.0	0.0018	0.0020	0.0021	0.0017	0.0016	0.0016
C16	0.2928	0.1915	−0.3941	1.0000	0.0571	0.0445	0.0416	0.0207	0.0268	0.0128
	0.0003	0.0004	0.0004	0.0	0.0019	0.0016	0.0017	0.0014	0.0015	0.0014
C17	0.1652	0.1512	−0.3997	1.0000	0.0186	0.0531	0.0377	0.0218	0.0094	0.0136
	0.0003	0.0004	0.0004	0.0	0.0018	0.0018	0.0016	0.0014	0.0013	0.0014
C18	0.1387	0.0957	−0.2671	1.000	0.0321	0.0466	0.0405	0.0183	0.0132	0.0125
	0.0003	0.0003	0.0003	0.0	0.0014	0.0016	0.0016	0.0013	0.0012	0.0012
C19	0.0736	0.1812	0.1703	1.0000	0.0276	0.0402	0.0366	0.0132	0.0143	0.0152
	0.0002	0.0003	0.0003	0.0	0.0013	0.0014	0.0014	0.0012	0.0011	0.0011
C20	0.0291	0.5641	0.4781	1.0000	0.0629	0.1201	0.0723	0.0296	0.0271	0.0456
	0.0004	0.0006	0.0006	0.0	0.0027	0.0011	0.0029	0.0029	0.0022	0.0029
HC2	0.4091	−0.0235	0.2693	1.0000	0.0550					
	0.0033	0.0037	0.0039	0.0	0.0093					
HC3	0.6134	0.1355	0.4719	1.0000	0.0775					
	0.0038	0.0039	0.0044	0.0	0.0101					
HC4	0.6752	0.4104	0.5219	1.0000	0.0550					
	0.0036	0.0038	0.0042	0.0	0.0094					
HC5	0.5378	0.5000	0.3565	1.0000	0.0569					
	0.0035	0.0041	0.0042	0.0	0.0103					
HC6	0.3429	0.3364	0.1447	1.0000	0.0782					
	0.0039	0.0043	0.0047	0.0	0.0117					

(continued on facing page)

TABLE II. *(continued)*

Atom	X/A	Y/B	Z/C	K	U11	U22	U33	U23	U13	U12
HC8	0.1423	−0.2151	0.1662	1.0000	0.0494					
	0.0031	0.0034	0.0039	0.0	0.0087					
HC9	0.1398	−0.4595	0.1678	1.0000	0.0705					
	0.0038	0.0042	0.0047	0.0	0.0115					
HC10	0.2143	−0.5724	−0.0316	1.0000	0.0603					
	0.0044	0.0049	0.0054	0.0	0.0142					
HC11	0.2832	−0.4268	−0.1989	1.0000	0.1040					
	0.0046	0.0049	0.0055	0.0	0.0147					
HC12	0.2749	−0.1975	−0.1845	1.0000	0.0617					
	0.0026	0.0029	0.0032	0.0	0.0066					
HC14	0.4353	0.1272	−0.0685	1.0000	0.0534					
	0.0033	0.0034	0.0039	0.0	0.0087					
HC15	0.4839	0.2180	−0.2728	1.0000	0.0719					
	0.0043	0.0045	0.0050	0.0	0.0128					
HC16	0.3079	0.2285	−0.4739	1.0000	0.0546					
	0.0038	0.0042	0.0048	0.0	0.0114					
HC17	0.0910	0.1589	−0.4651	1.0000	0.0524					
	0.0041	0.0043	0.0050	0.0	0.0116					
HC18	0.0519	0.0607	−0.2643	1.0000	0.0463					
	0.0038	0.0039	0.0044	0.0	0.0102					

TABLE III. Available Bond Distances (A) and Relevant Standard Deviations (S.D.) for the Cyanogen Molecule.

r(C–C)	(S.D.)	r(C≡N)	(S.D.)	Method	Ref.
1.37	(0.02)	1.16	(0.02)	Electron diffraction	10 a
1.38	(0.02)	1.15	(0.02)	Electron diffraction	12
1.38_9	(0.030)	1.15_4	(0.017)	Rotational anal. i.r.	13
1.387_1	(0.001_4)	1.155_2	(0.001_3)	Electron diffraction	10 b
1.37	(0.02)	1.13	(0.02)	X-ray single crystal	14
1.381	(0.008)	1.127	(0.008)	X-ray single crystal	this work

Mass spectra revealed that C_2N_2 is rapidly released at *ca.* 80 °C from (*2*) *in vacuo* and TG analysis showed very clearly that (*2*) loses the weight expected (±2%) for the release of 1 mol of C_2N_2 per mol of (*2*) at *ca.* 100 °C.

The crystal structure of (*2*) has been established by X-ray diffraction using the Patterson–Fourier method. The structure has been refined by full matrix least squares, employing thermal anisotropic parameters for non-hydrogen atoms. Hydrogen atoms were detected in the Fourier difference map and isotropically refined during the last refinement cycle**. The molecular structure of (*2*) and a view of part of the unit cell are reported in Figs. 1 and 2. Some important molecular and intermolecular parameters are reported in Table I.

The X-ray analysis reveals that (*2*) contains planar $[Ni(CN)_2(PPh_3)_2]$ complexes lying at definitely nonbonding distances with respect to the C_2N_2 trapped molecules. No other X-ray structure of $[Ni(CN)_2L_2]$ complexes has been determined so far, so that the essential interatomic bond distances found for (*2*) have to be compared with data referring to a number of compounds containing the ion $[Ni(CN)]_4^{2-}$ [3–5]. The average values for the Ni–C and C≡N bond distances in these compounds are 1.85 and 1.16 Å respectively, while the corresponding average values for five different Hofmann-type clathrates are 1.86 and 1.15 Å [6, 7]. It is seen that the Ni–C (1.873 Å) and C≡N (1.155 Å) distances in (*2*) appear quite

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***Crystal data*: $[Ni(CN)_2(PPh_3)_2]\cdot(C_2N_2)$, M = 687.36: triclinic, space group $P\bar{1}$, a = 11.318(4), b = 9.587(5), c = 9.137(5) Å; α = 99.9(0.1)°, β = 107.2(0.1)°, γ = 108.8(0.1)°, U = 857(1) $Å^3$, Z = 1; D_c = 1.33 g cm^{-3}; F(000) = 356. Graphite-monochromatized Mo Kα radiation, λ = 0.71069 Å. 2677 reflections, having $I \geqslant 3\sigma(I)$, were measured in the range $4° < 2\theta < 50°$ with a fully automated Philips PW 1110 four circle diffractometer. The final R-factor evaluated on 2677 reflections was 3.9%. All the calculations were performed by using the SHELX programs. The atomic fractional coordinates and thermal parameters are reported in Table II.

normal, as in the Ni–P bond distance (2.225 Å) if it is compared with the value 2.28 Å found for [$NiCl_2(PPh_3)_2$] [8a] and 2.333 Å (average) observed for [$NiBr_2(PPh_3)_2$] [8b]. Bond angles at the phosphorus atoms compare well with those referring to related Ni(II) complexes [9].

The data reported here for (*2*) clearly indicate that the molecular lattice formed by the repetition of the *trans*-[$Ni(CN)_2(PPh_3)_2$] complex contains fairly wide channels defined by two phenyl rings and by two Ni–C≡N 'sticks', the 'diameter' of the channels being roughly 8 Å. This value is close to those found in thiourea (7.0 Å) and in urea (6.0 Å) clathrates [10] and leaves enough room for the allocation of the C_2N_2 molecules.

The molecular geometry and the bond distances and angles for C_2N_2 reported in the literature are based on an electron diffraction study [11] and on rotational spectrometric measurements [12–14] in the gas phase, as well as on an X-ray single crystal diffraction study carried out in 1963 [15]. All available bond distances data are collected in Table III.

It is seen that our data agree with those obtained by the same technique [15], but they are apparently more accurate. On the other hand our data, particularly those referring to the C≡N distance, appear in agreement with those obtained from the electron diffraction studies and from rotational spectroscopy, if the correction for the riding motion [16] is considered (C≡N distance 1.151(8) Å).

References

1 B. Corain, *Coord. Chem. Rev., 47,* 165 (1982).
2 P. Rigo and A. Turco, *Coord. Chem. Rev., 13,* 133 (1974).
3 S. S. Basson, L. O. C. Bok and J. G. Leipoldt, *Acta Cryst., B25,* 579 (1969).
4 J. G. Leipoldt, S. S. Basson and L. D. C. Bok, *Acta Cryst., B26,* 361 (1970).
5 L. D. C. Bok, S. S. Basson, J. G. Leipoldt and G. F. S. Wessels, *Acta Cryst., B27,* 1233 (1971).
6 T. Iwamoto, T. Miyoshi and Y. Sasaki, *Acta Cryst., B30,* 292 (1974).
7 R. Kuroda and Y. Sasaki, *Acta Cryst., B30,* 687 (1974).
8 a) G. Garton, D. E. Henn, N. M. Powell and L. M. Venanzi, *J. Chem. Soc.,* 3625 (1963).
b) J. A. J. Jarvis, R. H. B. Mais and P. G. Owston, *J. Chem. Soc., A,* 1473 (1968).
9 a) B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. A,* 1688 (1970).
b) J. A. J. Arvis, R. H. B. Mars and P. G. Owston, *J. Chem. Soc. A,* 1473 (1968).
10 J. E. D. Davies, *J. Chem. Ed., 54,* 536 (1977).
11 a) L. Pauling, H. D. Spingall and K. J. Palmer, *J. Am. Chem. Soc., 61,* 927 (1939).
b) Y. Morino, K. Kuchitsu, Y. Hori and M. Tanimoto, *Bull. Chem. Soc. Japan, 41,* 2349 (1968).
12 G. D. Craine and H. W. Thompson, *Trans. Far. Soc., 49,* 1273 (1953).
13 C. K. Mфller and B. T. Stoicheff, *Canad. J. Phys., 82,* 630 (1954).
14 A. G. Maki, *J. Chem. Phys., 43,* 3193 (1965).
15 A. S. Parkes and R. E. Huges, *Acta Cryst., 16,* 734 (1963).
16 W. R. Busing and H. A. Levy, *Acta Cryst., 17,* 142 (1964).