Structure of *trans*-M(CO)(C₄N₃)(PPh₃)₂.1.5C₆H₆ (M = Ir and Rh): the Pyramidal Geometry of the Tricyanomethanide Anion (C₄N₃⁻)

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Abstract

The crystal structures of two tricyanomethanide (TCM) complexes have been determined. Compound (1), *trans*-bis(triphenylphosphine)carbonyl(2,2-dicyanoethylideneamino)iridium(I) (the ligand 2,2-dicyanoethylideneamino = TCM), was studied at both 298 K (RT) and 135 K (LT). Crystal data: triclinic, a = 11.549 (3), b = 12.528 (2), c = 16.931 (2) Å, α = 91.13 (1), β = 99.45 (2), γ = 114.87 (2)°, final R = 0.039 and wR = 0.054 for the RT structure, and triclinic, a = 11.330 (4), b = 12.337 (4), c = 16.908 (4) Å, α = 91.61 (2), β = 99.60 (3), γ = 114.48 (3)°, final R = 0.036 and wR = 0.046 for the LT structure. The RT structure of (2), *trans*-bis(triphenylphosphine)carbonyl(2,2-dicyanoethylideneamino)rhodium(I), is very similar to the RT structure of (1). Crystal data: triclinic, a = 11.759 (3), b = 11.779 (5), c = 16.352 (3) Å, α = 102.21 (2), β = 104.61 (2), γ = 94.92 (3)°, final R = 0.070 and wR = 0.079. In both cases the TCM ligand is coordinated to the metal, near linearly through nitrogen, and both metal centers have a distorted square-planar geometry. In the RT structure, the geometry of TCM is planar with one set of unusually large displacement parameters for one of the cyano groups. In the LT structure of (1), these large anisotropic displacement parameters were resolved into half-populated C and N sites of disordered cyano groups. The geometry of TCM is thus slightly pyramidal, with the central C atoms lying 0.115 Å out of the plane defined by the three C atoms (C1, C2, C431) bonded to it.

Introduction

The tricyanomethanide anion (TCM) can coordinate to transition metals through its N end [⁻N═C═C(CN)₂] with apparent planar geometry. The title

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Table 1. *Experimental details*

	trans-Ir(CO)(C₄N₃)-(PPh₃)₂.1.5C₆H₆ (1)	*trans*-Rh(CO)(C₄N₃)-(PPh₃)₂.1.5C₆H₆ (2)	
Temperature (K)	298	135	298
Crystal system	Triclinic	Triclinic	Triclinic
M_r		862.74	952.04
Space group	P1̄	P1̄	P1̄
a (Å)	11.549 (3)	11.330 (4)	11.759 (3)
b (Å)	12.528 (2)	12.337 (4)	11.779 (5)
c (Å)	16.931 (2)	16.908 (4)	16.352 (3)
α ( )	91.13 (1)	91.61 (2)	102.21 (2)
β ( )	99.45 (2)	99.60 (2)	104.61 (2)
γ ( )	114.87 (2)	114.48 (3)	94.92 (3)
V (Å³)	2181.5 (7)	2108.4 (12)	2118.9 (21)
Z	2	2	2
D_x	1.449	1.500	1.352
λ (Mo $K\alpha$) (Å)		0.71073	0.71073
No. of reflections for lattice parameters	25	25	25
θ range for lattice parameters ( )	10–15.5	11–15	9–12.5
μ (mm⁻¹)	3.16	3.27	0.51
Crystal color	Yellow	Yellow	Yellow
Crystal size (mm)	0.25 × 0.28 × 0.50	0.40 × 0.48 × 0.63	0.15 × 0.15 × 0.20
Diffractometer type		Enraf–Nonius CAD-4	
Data collection method		θ/2θ scans	
Absorption correction type	Empirical	ψ scans	
Transmission min.–max.	0.746–1.00	0.641–1.00	0.821–1.00
Standard reflections	3, every 72000 s	3, every 10000 s	3, every 3600 s
Variation of standards (%)	~6	~12.1	~40
Measured reflections	8061	9248	5850
Independent reflections	7676	9118	5514
Observed reflections [$I > 3\sigma(I)$]	6359	8160	2818
2θ range ( )	2–50	2–54	2–45
hkl range	−13 < h < 12 0 < k < 14 −20 < l < 20	0 < h < 14 −15 < k < 14 −21 < l < 21	−12 < h < 12 0 < k < 12 −17 < l < 17
Refinement based on	F	F	F
R, wR	0.039, 0.054 0.039, 0.055*	0.036, 0.046	0.070, 0.079
S	1.762 1.809*	2.190	2.276
$(\Delta/\sigma)_{max}$	0.04 0.05*	0.05	0.03
No. of parameters refined	265 263*	275	279
$\Delta\rho$ (e Å⁻³)	−0.994, 0.986 −0.950, 0.968*	−1.665, 1.464	−1.363, 0.776
w		$4F_c^2/[\sigma^2(I) + (0.02F_c^2)^2]$	
Source of atomic scattering factors		*International Tables for X-ray Crystallography* (1974, Vol. IV)	

* Values for disordered model of the RT structure of (1).

compounds, *trans*-Ir(CO)(PPh₃)₂(TCM) (1) and *trans*-Rh(CO)(PPh₃)₂(TCM) (2), were the first reported examples of monomeric N-end TCM–transition-metal complexes (Lenarda & Baddley,

1972). The crystal structure of (1) has been studied (Witt, 1973; Wang, 1987) and it was observed that one of the cyano groups has unusually large displacement parameters. In previous structural studies of TCM complexes, TCM served either as a bridging ligand (Konnert & Britton, 1966; Biondi, Bonamico, Torelli & Vaciage, 1965; Chow & Britton, 1975; Summerville, Cohen, Hatano & Scheidt, 1978; Britton & Chow, 1983) or as an uncoordinated anion (Baukova, Kravtsov, Kuz'mina, Dvortsova, Poray-Koshits & Perevalova, 1989). Details of the structures of the monomeric TCM–transition-metal complexes have not been reported. To clarify this unusual pyramidal geometry of TCM, we report both room-temperature (RT) and low-temperature (LT) crystal structures of *trans*-Ir(CO)(PPh₃)₂(TCM) (1) and the room-temperature structure of its Rh analogue (2). An attempt to collect low-temperature data for (2) was unsuccessful as the crystals were destroyed by cooling.

Experimental

The title compounds were synthesized according to the procedure of Lenarda & Baddley (1972). Crystals suitable for X-ray analysis were grown from hot benzene. A yellow crystal of compound (1) (for both the room-temperature and low-temperature measurements) was sealed in a capillary tube. The same sampling procedure was used for compound (2). Intensities for (2) decayed 40% during data collection. Therefore, a linear decay correction was applied during data reduction. Table 1 lists data-collection details for compounds (1) and (2).*

The structures of (1) and (2) were both solved by heavy-atom methods using *Personal SDP* (Frenz, 1989). Atomic scattering factors including anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structures were refined by full-matrix least squares, and $\sum w(|F_o| - |F_c|)^2$ was minimized. One of the cyano groups (C3—N3) showed very large displacement parameters for both [(1) and (2)] room-temperature structures indicating that this group might be disordered. Indeed, two resolved peaks were observed for N3 in a difference Fourier map using the low-temperature data. Hence, C3—N3 was refined as two half-populated disordered groups in

* Lists of structure factors, anisotropic displacement parameters, H-atom positional parameters, and bond distances and angles of all three structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71001 (115 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0435]

the LT structure. This disordered model was also applied to the RT structure of (1). The results show that both ordered and disordered models fit the room-temperature data. The site occupancy factors of the disordered cyano group were refined. The final values were close to 0.5 [0.49 (1) and 0.51 (1) for the RT structure and 0.47 (1) and 0.53 (1) for the LT structure]. Therefore, the equal population disordered model was used for both RT and LT structures. The refinement results of (1) are also presented in Table 1.

One of the benzene solvent molecules co-crystallized with compound (1) was also disordered. The 12 C atoms with an occupancy factor of 0.5 on the disordered benzene solvent molecule were idealized to two regular hexagons (with C—C = 1.395 Å) using *SHELX*76 (Sheldrick, 1976). Both positional and displacement parameters of these C atoms in the RT structure were fixed at an idealized geometry during the least-squares refinements, but the displacement parameters of these C atoms in the LT structure were refined. All H atoms, except those on the solvent molecule, were placed at idealized positions with fixed displacement parameters. These H atoms were included in the structure-factor calculations but were not refined. The atomic displacement parameters at 135 K are, in general, about 50% less than those at 298 K except for the disordered cyano group, C3—N3. Most of the calculations were carried out on a 80386-based IBM-compatible PC. The *SHELX*76 computations were done on an IBM4361 mainframe computer. Final positional parameters for the RT and LT structures of (1) and for structure (2) are presented in Tables 2 and 3.

Results and discussion

Crystal structure of (1)

An *ORTEP* drawing (Johnson, 1970; Frenz, 1989) and atomic labeling scheme are shown in Fig. 1 for both the RT and LT structures. The Ir atom lies 0.090 (1) Å [0.091 (1) Å for the LT structure] below the least-squares molecular plane containing P1, P2, N1 and C10, and none of these four atoms deviates more than 0.056 (7) Å [0.044 (1) Å for LT] from the plane. The coordination geometry about the Ir atom is distorted square planar. The PPh₃ groups are *trans* to each other with Ir—P distances of 2.319 (1) and 2.317 (1) Å [2.3173 (8) and 2.3178 (8) Å for LT]. The Ir—CO bond length is 1.800 (5) Å [1.840 (3) Å for LT], and the Ir—N bond distance is 2.032 (4) Å [2.046 (3) Å for LT]. Selected bond distances and bond angles are presented in Tables 4 and 5, respectively.

trans-$M(CO)(C_4N_3)(PPh_3)_2 \cdot 1.5C_6H_6$ ($M =$ Ir AND Rh)

Table 2. *Positional parameters* (*with e.s.d.'s in parentheses*) *for* (1)

First and second rows are parameters for the RT and LT structures respectively. Parameters without e.s.d.'s were not refined. $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq} (Å²)		x	y	z	B_{eq} (Å²)
Ir1	0.32764 (2)	0.16181 (2)	0.25027 (1)	3.414 (5)	C42	0.0544 (7)	0.0338 (6)	0.3850 (5)	5.7 (2)*
	0.32751 (1)	0.16107 (1)	0.24944 (1)	1.610 (3)		0.0537 (5)	0.0302 (4)	0.3875 (3)	2.54 (8)*
P1	0.4199 (1)	0.0963 (1)	0.15981 (9)	3.41 (3)	C43	−0.0671 (7)	−0.0527 (7)	0.3955 (5)	6.1 (2)*
	0.4200 (1)	0.09358 (9)	0.15809 (6)	1.46 (2)		−0.0650 (5)	−0.0574 (4)	0.3981 (3)	2.75 (9)*
P2	0.2197 (1)	0.2308 (1)	0.32668 (9)	3.64 (3)	C44	−0.1774 (8)	−0.0468 (7)	0.3594 (5)	7.0 (2)*
	0.2195 (1)	0.23148 (9)	0.32796 (7)	1.51 (2)		−0.1817 (5)	−0.0532 (5)	0.3622 (3)	3.07 (9)*
O10	0.5384 (5)	0.4044 (5)	0.2696 (4)	7.5 (2)	C45	0.1748 (8)	0.0386 (8)	0.3126 (6)	7.8 (2)*
	0.5408 (4)	0.4085 (3)	0.2678 (2)	3.07 (8)		−0.1800 (5)	0.0367 (5)	0.3152 (4)	3.4 (1)*
N1	0.1799 (4)	−0.0036 (4)	0.2300 (3)	4.4 (1)	C46	−0.0534 (7)	0.1267 (7)	0.3005 (5)	6.0 (2)*
	0.1772 (3)	−0.0079 (3)	0.2294 (2)	1.93 (8)		−0.0600 (5)	0.1246 (4)	0.3032 (3)	2.56 (8)*
N2	0.0064 (7)	−0.3274 (5)	0.0648 (4)	7.1 (2)	C51	0.1940 (5)	0.3490 (5)	0.2781 (4)	4.3 (1)*
	−0.0056 (5)	−0.3315 (4)	0.0580 (3)	3.3 (1)		0.1914 (4)	0.3526 (4)	0.2816 (3)	1.88 (7)*
N3	−0.161 (1)	−0.321 (1)	0.2734 (6)	22.5 (4)	C52	0.1656 (7)	0.3366 (7)	0.1937 (5)	6.0 (2)*
N31†	−0.103 (1)	−0.3500 (9)	0.3018 (6)	4.0 (2)*		0.1702 (5)	0.3471 (4)	0.1973 (3)	2.56 (8)*
N32†	−0.171 (1)	−0.322 (1)	0.2722 (8)	5.9 (3)*	C53	0.1462 (8)	0.4282 (7)	0.1537 (5)	7.0 (2)*
C1	0.1022 (5)	−0.0988 (5)	0.2131 (4)	4.1 (1)		0.1526 (5)	0.4385 (5)	0.1579 (3)	2.93 (9)*
	0.1012 (4)	−0.1049 (4)	0.2142 (3)	1.96 (9)	C54	0.1588 (8)	0.5243 (8)	0.1965 (6)	7.4 (2)*
C2	0.0074 (6)	−0.2760 (5)	0.1220 (4)	4.7 (2)		0.1567 (5)	0.5359 (5)	0.2017 (3)	3.05 (9)*
	0.0019 (4)	−0.2828 (4)	0.1186 (4)	2.18 (9)	C55	0.1801 (9)	0.5355 (8)	0.2760 (6)	8.0 (2)*
C3	−0.084 (1)	−0.2702 (9)	0.2384 (6)	11.5 (3)		0.1731 (5)	0.5408 (5)	0.2849 (3)	3.2 (1)*
C431†	−0.0497 (8)	−0.2967 (8)	0.2554 (6)	2.2 (2)*	C56	0.1989 (7)	0.4477 (7)	0.3201 (5)	6.1 (2)*
C432†	−0.089 (1)	−0.276 (1)	0.2355 (7)	3.2 (2)*		0.1908 (5)	0.4494 (4)	0.3251 (3)	2.54 (8)*
C4	0.0098 (6)	−0.2138 (6)	0.1918 (4)	5.1 (2)	C61	0.3008 (6)	0.2882 (5)	0.4305 (4)	4.3 (1)*
	0.0111 (4)	−0.2233 (4)	0.1931 (3)	2.3 (1)		0.3059 (4)	0.2900 (4)	0.4315 (3)	1.91 (7)*
C10	0.4573 (6)	0.3089 (5)	0.2635 (4)	4.7 (2)	C62	0.2376 (7)	0.3141 (6)	0.4848 (5)	5.6 (2)*
	0.4604 (4)	0.3138 (4)	0.2613 (3)	2.13 (9)		0.2440 (4)	0.3167 (4)	0.4889 (3)	2.40 (8)*
C11	0.3034 (5)	0.0484 (5)	0.0653 (3)	3.6 (1)*	C63	0.3083 (8)	0.3609 (7)	0.5653 (5)	6.7 (2)*
	0.3006 (4)	0.0437 (4)	0.0635 (3)	1.73 (6)*		0.3137 (5)	0.3642 (5)	0.5671 (3)	2.82 (9)*
C12	0.2554 (6)	−0.0631 (5)	0.0248 (4)	4.6 (1)*	C64	0.4289 (8)	0.3777 (7)	0.5859 (5)	6.9 (2)*
	0.2514 (4)	−0.0704 (4)	0.0232 (3)	2.09 (7)*		0.4446 (5)	0.3835 (5)	0.5881 (3)	2.79 (9)*
C13	0.1616 (7)	−0.0923 (7)	−0.0451 (5)	6.3 (2)*	C65	0.4910 (7)	0.3507 (7)	0.5333 (5)	6.6 (2)*
	0.1548 (5)	−0.1031 (4)	−0.0472 (3)	2.75 (9)*		0.5052 (5)	0.3540 (4)	0.5327 (3)	2.76 (9)*
C14	0.1155 (7)	−0.0133 (7)	−0.0754 (5)	6.2 (2)*	C66	0.4281 (6)	0.3052 (6)	0.4553 (4)	5.2 (1)*
	0.1090 (5)	−0.0209 (5)	−0.0785 (3)	2.80 (9)*		0.4372 (4)	0.3072 (4)	0.4543 (3)	2.16 (7)*
C15	0.1641 (7)	0.0963 (7)	−0.0346 (5)	6.4 (2)*	C71	0.4189 (9)	0.4547 (9)	−0.0746 (6)	8.6 (2)*
	0.1576 (5)	0.0924 (5)	−0.0381 (3)	2.84 (9)*		0.4136 (6)	0.4520 (5)	−0.0735 (4)	3.6 (1)*
C16	0.2569 (6)	0.1288 (6)	0.0362 (4)	5.5 (2)*	C72	0.4449 (9)	0.4845 (9)	0.0675 (6)	8.3 (2)*
	0.2521 (4)	0.1248 (4)	0.0334 (3)	2.47 (8)*		0.4511 (5)	0.4851 (5)	0.0713 (4)	3.5 (1)*
C21	0.4582 (5)	−0.0275 (5)	0.1858 (4)	3.8 (1)*	C73	0.3729 (9)	0.4463 (8)	−0.0025 (6)	8.2 (2)*
	0.4604 (4)	−0.0313 (4)	0.1834 (3)	1.79 (7)*		0.3657 (5)	0.4377 (5)	−0.0020 (4)	3.6 (1)*
C22	0.5261 (6)	−0.0631 (6)	0.1393 (4)	5.1 (1)*	C81	0.712	0.246	0.445	10.00
	0.5310 (4)	−0.0679 (4)	0.1374 (3)	2.36 (8)*		0.280	−0.236	0.550	5.9 (4)*
C23	0.5532 (7)	−0.1590 (7)	0.1585 (5)	6.0 (2)*	C82	0.799	0.249	0.514	10.00
	0.5603 (5)	−0.1639 (5)	0.1563 (3)	2.91 (9)*		0.202	−0.243	0.475	5.7 (3)*
C24	0.5130 (7)	−0.2152 (7)	0.2253 (5)	6.4 (2)*	C83	0.768	0.152	0.559	10.00
	0.5212 (5)	−0.2226 (4)	0.2224 (3)	2.75 (9)*		0.239	−0.145	0.430	5.5 (3)*
C25	0.4536 (7)	−0.1775 (7)	0.2729 (5)	6.3 (2)*	C84	0.651	0.051	0.535	10.00
	0.4548 (5)	−0.1854 (4)	0.2698 (3)	2.66 (8)*		0.354	−0.041	0.460	4.9 (3)*
C26	0.4216 (6)	−0.0831 (6)	0.2525 (4)	5.1 (1)*	C85	0.565	0.048	0.466	10.00
	0.4231 (4)	−0.0894 (4)	0.2508 (3)	2.13 (7)*		0.431	−0.035	0.535	5.4 (3)*
C31	0.5714 (5)	0.2043 (5)	0.1361 (4)	4.0 (1)*	C86	0.595	0.145	0.421	10.00
	0.5729 (4)	0.2039 (4)	0.1344 (3)	1.84 (7)*		0.394	−0.132	0.580	4.9 (3)*
C32	0.5821 (6)	0.2392 (6)	0.0592 (4)	5.2 (1)*	C811	0.693	0.206	0.445	10.00
	0.5817 (4)	0.2406 (4)	0.0579 (3)	2.29 (8)*		0.274	−0.232	0.568	6.8 (4)*
C33	0.6994 (7)	0.3215 (7)	0.0448 (5)	6.5 (2)*	C821	0.754	0.170	0.510	10.00
	0.7017 (5)	0.3260 (4)	0.0439 (3)	2.74 (8)*		0.216	−0.192	0.502	8.4 (5)*
C34	0.8040 (7)	0.3706 (7)	0.1054 (5)	6.6 (2)*	C831	0.870	0.252	0.558	10.00
	0.8111 (5)	0.3757 (5)	0.1052 (3)	2.95 (9)*		0.102	−0.273	0.450	7.9 (5)*
C35	0.7952 (8)	0.3370 (8)	0.1805 (6)	7.2 (2)*	C841	0.926	0.369	0.539	10.00
	0.8017 (5)	0.3393 (5)	0.1818 (3)	3.05 (9)*		0.046	−0.393	0.463	8.7 (6)*
C36	0.6789 (7)	0.2527 (6)	0.1979 (5)	5.8 (2)*	C851	0.865	0.404	0.474	10.00
	0.6835 (5)	0.2533 (4)	0.1961 (3)	2.62 (8)*		0.104	−0.433	0.529	7.5 (5)*
C41	0.0596 (5)	0.1238 (5)	0.3383 (4)	3.9 (1)*	C861	0.749	0.323	0.426	10.00
	0.0582 (4)	0.1226 (4)	0.3404 (3)	1.75 (6)*		0.218	−0.352	0.581	6.0 (4)*

* Refined isotropically. † The disordered model of the LT structure.

Table 3. *Positional parameters (with e.s.d.'s in parentheses) for (2)*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq} (Å^2)
Rh	0.3315 (1)	0.2450 (1)	0.21690 (7)	2.56 (2)
P1	0.4025 (3)	0.3699 (4)	0.1419 (2)	2.93 (9)
P2	0.2521 (3)	0.0932 (4)	0.2682 (2)	2.76 (9)
O10	0.0960 (9)	0.319 (1)	0.1704 (6)	5.4 (3)*
N1	0.4960 (9)	0.194 (1)	0.2396 (7)	3.8 (3)
N2	0.788 (1)	−0.024 (1)	0.2990 (9)	7.0 (4)
N3	0.839 (1)	0.289 (2)	0.201 (1)	12.0 (6)
C1	0.592 (1)	0.172 (1)	0.2456 (8)	3.5 (4)
C2	0.748 (1)	0.059 (2)	0.2794 (9)	5.1 (5)
C3	0.779 (1)	0.230 (2)	0.224 (1)	7.1 (6)
C4	0.706 (1)	0.152 (1)	0.2514 (9)	4.1 (4)
C10	0.190 (1)	0.287 (1)	0.1908 (8)	3.4 (3)*
C11	0.296 (1)	0.449 (1)	0.0829 (7)	2.6 (3)*
C12	0.243 (1)	0.530 (1)	0.1290 (8)	3.7 (3)*
C13	0.164 (1)	0.588 (2)	0.0855 (9)	4.9 (4)*
C14	0.136 (1)	0.571 (2)	−0.0020 (9)	4.9 (4)*
C15	0.188 (1)	0.493 (1)	−0.0488 (9)	4.4 (4)*
C16	0.271 (1)	0.431 (1)	−0.0056 (8)	3.4 (3)*
C21	0.529 (1)	0.483 (1)	0.2022 (8)	3.0 (3)*
C22	0.552 (1)	0.577 (1)	0.1637 (8)	3.9 (3)*
C23	0.651 (1)	0.663 (1)	0.2089 (9)	4.5 (4)*
C24	0.721 (1)	0.656 (1)	0.2865 (9)	4.7 (4)*
C25	0.700 (1)	0.569 (2)	0.326 (1)	6.0 (4)*
C26	0.601 (1)	0.483 (2)	0.2817 (9)	4.7 (4)*
C31	0.449 (1)	0.275 (1)	0.0579 (7)	2.5 (3)*
C32	0.560 (1)	0.293 (1)	0.0438 (8)	4.2 (3)*
C33	0.589 (1)	0.215 (2)	−0.0209 (9)	5.2 (4)*
C34	0.512 (1)	0.117 (1)	−0.0716 (9)	5.0 (4)*
C35	0.404 (1)	0.099 (1)	−0.0570 (9)	4.8 (4)*
C36	0.374 (1)	0.174 (1)	0.0074 (8)	3.6 (3)*
C41	0.361 (1)	0.004 (1)	0.3060 (7)	2.3 (3)*
C42	0.460 (1)	0.055 (1)	0.3739 (8)	3.5 (3)*
C43	0.546 (1)	−0.009 (1)	0.4046 (9)	4.4 (4)*
C44	0.538 (1)	−0.127 (2)	0.3647 (9)	5.2 (4)*
C45	0.441 (1)	−0.178 (2)	0.2961 (9)	5.6 (4)*
C46	0.352 (1)	−0.114 (1)	0.2659 (8)	4.0 (3)*
C51	0.186 (1)	0.130 (1)	0.3574 (7)	2.9 (3)*
C52	0.203 (1)	0.072 (1)	0.4239 (8)	4.6 (4)*
C53	0.143 (1)	0.100 (2)	0.4880 (9)	5.0 (4)*
C54	0.069 (1)	0.175 (1)	0.4863 (9)	5.0 (4)*
C55	0.044 (1)	0.229 (2)	0.420 (1)	6.1 (4)*
C56	0.105 (1)	0.203 (2)	0.355 (1)	5.9 (4)*
C61	0.137 (1)	−0.007 (1)	0.1826 (7)	2.9 (3)*
C62	0.152 (1)	−0.038 (1)	0.0992 (8)	3.7 (3)*
C63	0.070 (1)	−0.118 (1)	0.0310 (9)	4.2 (4)*
C64	−0.030 (1)	−0.168 (2)	0.0467 (9)	4.8 (4)*
C65	−0.047 (1)	−0.138 (2)	0.1263 (9)	4.9 (4)*
C66	0.035 (1)	−0.058 (1)	0.1968 (9)	4.2 (3)*
C71	0.394 (2)	0.464 (2)	0.433 (1)	9.2 (6)*
C72	0.436 (2)	0.395 (2)	0.488 (1)	9.4 (7)*
C73	0.538 (2)	0.429 (2)	0.555 (1)	11.2 (8)*
C81	0.802 (2)	0.332 (2)	0.514 (1)	11.0 (7)*
C82	0.801 (2)	0.268 (2)	0.577 (1)	11.0 (7)*
C83	0.873 (2)	0.295 (2)	0.658 (1)	11.0 (7)*
C84	0.951 (2)	0.398 (2)	0.690 (1)	10.2 (7)*
C85	0.949 (2)	0.461 (2)	0.629 (1)	9.8 (6)*
C86	0.883 (2)	0.429 (2)	0.549 (1)	9.9 (7)*

* Refined isotropically.

Crystal structure of (2)

Fig. 2 shows an *ORTEP* drawing and atomic labeling for (2). The coordination geometry about Rh is distorted square planar, similar to Ir in (1). The distances between Rh and coordinated atoms are: Rh—P, 2.332 (3) and 2.348 (3) Å; Rh—CO, 1.76 (1) Å; Rh—N, 2.044 (8) Å. Selected bond distances and angles are listed in Table 6.

Geometry of TCM

In the RT structure of (1), the geometry of TCM is essentially planar [the largest deviation from the

TCM least-squares plane is 0.004 (7) Å for C2] with unusually large displacement parameters for cyano group C3—N3 (Fig. 3). By contrast, in the LT structure, C3—N3 is clearly separated into two half-populated sites. One half cyano group lies below the N1—C1—C4—C2—N2 least-squares plane [N32 0.478 (1) and C432 0.286 (1) Å below], and the other half lies above this plane [N31 0.548 (1) and C431 0.365 (1) Å above]. The C431—C4—C432 angle is 26.3 (4)°. Thus the geometry of TCM in the LT
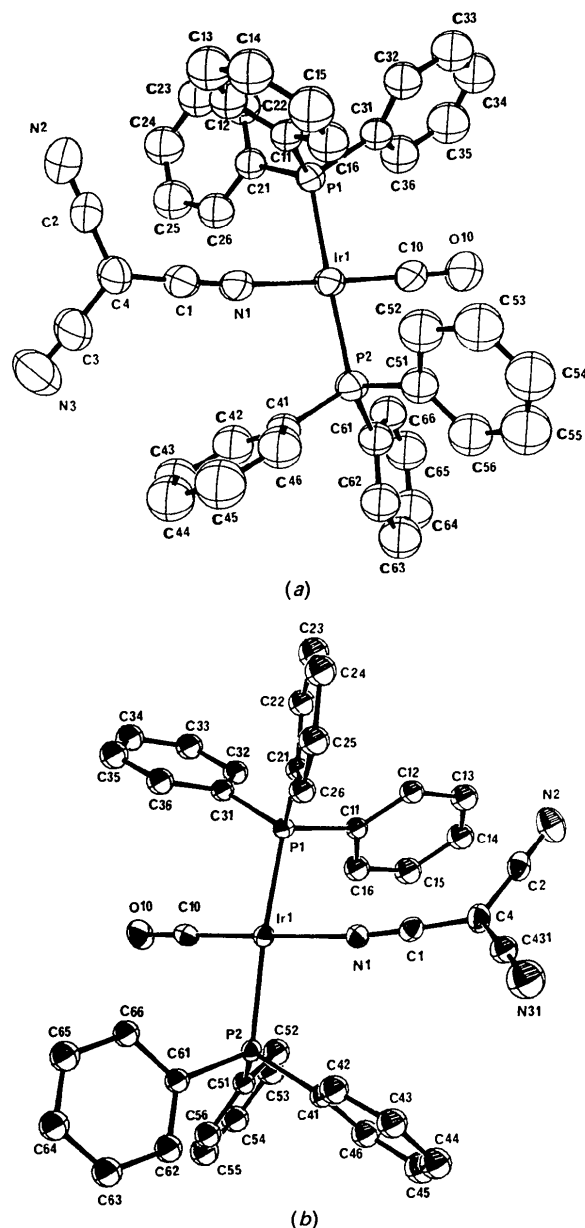

(*a*)

(*b*)

Fig. 1. *ORTEP* drawings of (1) with 50% probability ellipsoids for non-H atoms. (*a*) RT structure and (*b*) LT structure. Only one of the two half-populated CN positions is illustrated in the LT structure.

Table 4. *Bond distances (Å) (with e.s.d.'s in parentheses) for* (1)

Ir1—P1	2.319 (1) 2.3173 (8)	Ir1—P2	2.317 (1)† 2.3178 (8)*
Ir1—N1	2.032 (4) 2.046 (3)	Ir1—C10	1.800 (5) 1.840 (3)
P1—C11	1.819 (5) 1.817 (3)	P1—C21	1.826 (5) 1.822 (3)
P1—C31	1.821 (5) 1.822 (3)	P2—C41	1.817 (5) 1.817 (3)
P2—C51	1.815 (5) 1.823 (3)	P2—C61	1.823 (5) 1.822 (3)
O10—C10	1.157 (6) 1.133 (4)		

Geometry of TCM – ordered model

N1—C1	1.146 (6)	N2—C2	1.149 (7)
N3—C3	1.123 (9)	C1—C4	1.380 (7)
C2—C4	1.392 (8)	C3—C4	1.396 (9)

Geometry of TCM – disordered model

N1—C1	1.149 (7) 1.137 (4)	N2—C2	1.16 (1) 1.146 (5)
C1—C4	1.371 (8) 1.385 (4)	C2—C4	1.40 (1) 1.406 (5)
C4—C431	1.43 (2) 1.478 (8)	C4—C432	1.44 (2) 1.381 (9)
N31—C431	1.14 (2) 1.13 (1)	N32—C432	1.16 (2) 1.16 (1)

* LT bond distances.
† RT bond distances.

Table 5. *Selected bond and torsion angles (°) (with e.s.d.'s in parentheses) for* (1)

P1—Ir1—P2	172.83 (4) 173.36 (3)	Ir1—C10—O10	177.5 (6)† 178.9 (3)*
P1—Ir1—N1	86.2 (1) 86.20 (7)	P1—Ir1—C10	92.4 (2) 92.2 (1)
P2—Ir1—N1	92.7 (1) 92.75 (7)	P2—Ir1—C10	88.4 (2) 88.6 (1)
N1—Ir1—C10	177.5 (2) 176.7 (1)	Ir1—N1—C1	173.5 (4) 173.3 (3)
Ir1—P1—C11—C12	– 124.7 (5) – 124.2 (4)	Ir1—P1—C21—C22	– 173.0 (5) – 172.0 (3)
Ir1—P1—C31—C32	– 116.5 (5) – 115.3 (4)	Ir1—P2—C41—C42	69.7 (6) 70.0 (4)
Ir1—P2—C51—C52	36.8 (6) 32.1 (4)	Ir1—P2—C61—C62	– 169.7 (5) – 169.2 (3)

Geometry of TCM – ordered model

N1—C1—C4	179.1 (6)	N2—C2—C4	179.4 (7)
N3—C3—C4	176.5 (9)	C1—C4—C2	120.1 (5)
C1—C4—C3	121.6 (5)	C2—C4—C3	118.4 (5)

Geometry of TCM – disordered model

N1—C1—C4	179.1 (7) 177.6 (4)	N2—C2—C4	180 (2) 180.0 (7)
C1—C4—C2	120.2 (6) 120.1 (3)	C1—C4—C431	122.3 (8) 120.0 (4)
C1—C4—C432	118.8 (8) 120.2 (5)	C2—C4—C431	114.7 (8) 118.0 (4)
C2—C4—C432	118.8 (7) 118.2 (4)	C431—C4—C432	32 (1) 26.3 (4)
C4—C431—N31	171 (2) 175.1 (8)	C4—C432—N32	173 (2) 177 (1)

* LT angles.
† RT angles.

Table 6. *Selected bond distances (Å), angles (°) and torsion angles (°) (with e.s.d.'s in parentheses) for* (2)

Rh—P1	2.332 (3)	Rh—P2	2.348 (3)
Rh—N1	2.044 (8)	Rh—C10	1.76 (1)
P1—C11	1.833 (9)	P1—C21	1.83 (1)
P1—C31	1.812 (9)	P2—C41	1.802 (9)
P2—C51	1.813 (9)	P2—C61	1.805 (9)
O10—C10	1.18 (1)	N1—C1	1.16 (1)
N2—C2	1.19 (2)	N3—C3	1.13 (1)
C1—C4	1.36 (1)	C2—C4	1.36 (2)
C3—C4	1.42 (2)		
P1—Rh—P2	169.5 (1)	Rh—C10—O10	176.7 (9)
P1—Rh—N1	86.1 (2)	P1—Rh—C10	91.7 (3)
P2—Rh—N1	92.9 (2)	P2—Rh—C10	88.7 (3)
N1—Rh—C10	176.6 (4)	Rh—N1—C1	172.2 (8)
N1—C1—C4	176 (1)	N2—C2—C4	176 (2)
N3—C3—C4	178 (2)	C1—C4—C2	122 (1)
C1—C4—C3	118 (1)	C2—C4—C3	120 (1)
Rh—P1—C11—C12	64 (1)	Rh—P1—C21—C22	– 163.6 (9)
Rh—P1—C31—C32	– 129 (1)	Rh—P2—C41—C42	61 (1)
Rh—P2—C51—C52	– 140 (1)	Rh—P2—C61—C62	40 (1)

structure can be viewed as two pyramidal TCM half-anions superimposed on each other such that they share a triangular face containing C4 and two of the three cyano groups (C1—N1 and C2—N2; Fig. 4). The rationale behind this unusual pyramidal geometry of TCM is metal-to-ligand back-bonding. The TCM is σ-bonded to the Ir through N atoms, and the extra electron density on the metal back-donates to the π^* orbital of TCM. As a result of this back-bonding, electron density is localized on the central C atom of TCM and changes the TCM geometry from planar to slightly pyramidal.

The geometry of TCM in (2) is similar to that found in the RT structure of (1) with one of the cyano groups possessing unusually large displacement parameters. The structural similarity of (1) and (2) suggests that the geometry of TCM in (2) may also be pyramidal with a disordered cyano group.
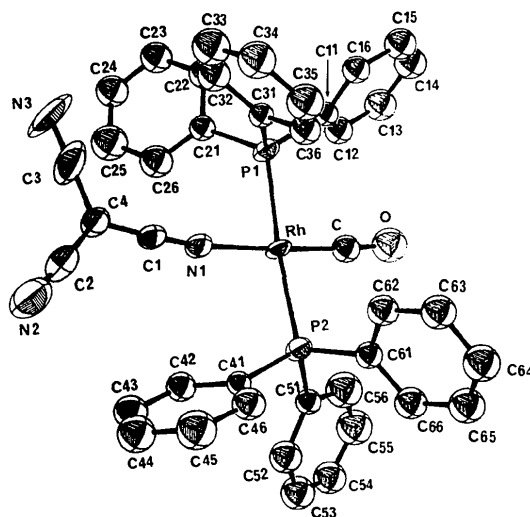

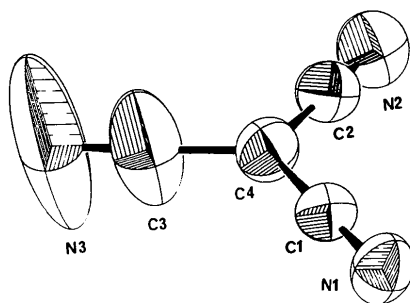Fig. 2. *ORTEP* drawing of (2) with 50% probability ellipsoids for non-H atoms.

Fig. 3. *ORTEP* drawing of the TCM ligand with 50% probability ellipsoids for the RT determination of compound (1).
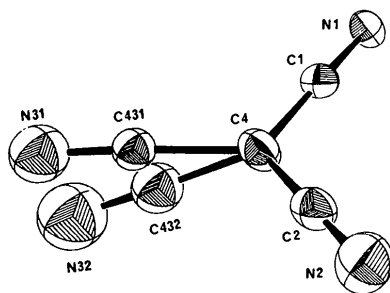

Fig. 4. *ORTEP* drawing of TCM with 50% probability ellipsoids for the LT determination of compound (1).

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Structures at 293 and 100 K of β-Tetrakis[bis(ethylenedithio)tetrathiafulvalene] Tetracyanonickelate(II): β-[BEDT-TTF]₄[Ni(CN)₄]

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Abstract

$[C_{10}H_8S_8]_4[Ni(CN)_4]$, $M_r = 1701.53$, $F(000) = 864$, $\lambda(Mo\ K\alpha) = 0.71073$ Å. At 293 K: triclinic, $P\bar{1}$, $a = 9.677\ (7)$, $b = 10.960\ (6)$, $c = 16.392\ (8)$ Å, $\alpha = 95.95\ (5)$, $\beta = 97.85\ (5)$, $\gamma = 115.13\ (5)°$, $V = 1533\ (4)$ Å³, $Z = 1$, $D_x = 1.842\ \text{g cm}^{-3}$, $\mu = 14.06\ \text{cm}^{-1}$, $R = 0.031$ based on 3565 observed reflections with $I \geq 6\sigma(I)$. At 100 K: triclinic, $P\bar{1}$, $a = 9.721\ (4)$, $b = 10.761\ (4)$, $c = 16.431\ (5)$ Å, $\alpha = 95.87\ (3)$, $\beta = 98.17\ (4)$, $\lambda = 115.71\ (3)°$, $V = 1507\ (2)$ Å³, $Z = 1$, $D_x = 1.875\ \text{g cm}^{-3}$, $\mu = 14.31\ \text{cm}^{-1}$, $R = 0.082$ based on 3865 observed reflections with $I \geq 6\sigma(I)$. The C atoms of the terminal ethylenic groups of each independent BEDT-TTF molecule are statistically distributed on both sides of the molecular mean plane at room temperature. This phenomenon disappears at 100 K where the BEDT-TTF molecules adopt different conformations. The organic molecules develop tetramerized stacks along the [210] direction. The structure belongs to the β type of the BEDT-TTF series.

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