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Tetracyanoethylene Complexes of Ni(0) and Co(−1) Containing Isocyanides and Nitrosyl

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Synopsis. The magnetic equivalence of the isocyanides in Ni(RNC)$_3$(TCNE) and Co(NO)(RNC)$_2$(TCNE) is more likely to be due to the free rotation of TCNE in solution than to the dissociative exchange of ligands.

Many phosphine and/or carbonyl complexes of transition metals are known to react with tetracyanoethylene (TCNE) to afford complexes with a rigidly bonded TCNE.[1,2] Recently we have reported for the first time the free rotation of TCNE in its adducts with some tetrakis(isocyanide)rhodium salts.[3] On the other hand, activated olefins were found to replace one molecule of phosphine from tetrahedral tris(triphenylphosphine)-(nitrosyl)-cobalt, -rhodium, and -iridium to form a square pyramidal complex with the rigidly bonded TCNE in the basal plane.[4] In connection with these results, it seemed that it would be of interest to investigate the reactions of TCNE with tetrahedral nickel- and cobalt-isocyanide complexes.[5,6]

Here we wish to report the synthesis and some spectroscopic studies of two types of complexes, Ni(RNC)$_3$(TCNE) and Co(NO)(RNC)$_2$(TCNE).

Experimental

All the tetrakis(isocyanide)nickel[5] and bis(isocyanide)-(carbonyl)(nitrosyl)cobalt[6] complexes were synthesized by the literature methods, including the previously unknown 2,4,6-trimethylphenyl isocyanide complexes. The reactions were carried out under nitrogen, and the recrystallizations were done in air, unless otherwise noted.

*Preparation of Tris(*p*-methoxyphenyl isocyanide)(tetracyanoethylene)nickel, Ni(*p*-$CH_3OC_6H_4NC$)$_3$,(TCNE) (1a).* TCNE (128 mg, 1 mmol) was added to a stirred suspension of Ni(p-$CH_3OC_6H_4NC$)$_4$ (592 mg, 1 mmol) in petroleum ether (20 ml). The color of the suspension gradually changed from bright yellow to brown. The suspension was then stirred overnight at the ambient temperature. The resultant powder was filtered and recrystallized from CH_2Cl_2/petroleum ether to yield black crystals of **1a** (350 mg, 61%).

Other nickel complexes were prepared in similar manners. Only the 2,4,6-$(CH_3)_3C_6H_2NC$ complex was recrystallized from ligroin.

*Preparation of Bis(*p*-methoxyphenyl isocyanide)(nitrosyl)(tetracyanoethylene)cobalt, Co(NO)(*p*-$CH_3OC_6H_4NC$)$_2$(TCNE) (2a).* A reaction of Co(NO)(CO)(p-$CH_3OC_6H_4NC$)$_2$ (383 mg, 1 mmol) with TCNE (128 mg, 1 mmol) in a manner similar to that described for **1a** afforded a brown powder, which was then filtered and recrystallized from CH_2Cl_2/petroleum ether under nitrogen to yield brown crystals of **2a** (310 mg, 64%).

Other cobalt complexes were obtained in analogous manners; only the p-ClC_6H_4NC complex was recrystallized from C_6H_6/petroleum ether under nitrogen.

The physical measurements were performed as has been described elsewhere.[3a] The analytical data and molecular weights of the complexes are collected in Table 1, and the IR and PMR data are summarized in Table 2.

Results and Discussion

The tetrakis(aryl isocyanide)nickel series reacts with an equimolar amount of TCNE to give tris(isocyanide)-(tetracyanoethylene)nickel, with the substitution of one molecule of isocyanide, as has been reported for the t-butyl isocyanide analog.[7] Bis(isocyanide)(carbonyl)-(nitrosyl)cobalt also reacts with TCNE to afford bis-(isocyanide)(nitrosyl)(tetracyanoethylene)cobalt, with the evolution of carbon monoxide. All the TCNE complexes of Ni and Co are dark brown or black in color and are stable in air in the solid state over an extended period of time. Some of them are, however, unstable in solution and were recrystallized under nitrogen.

Table 1. Analytical data and molecular weights of complexes

No.	Complexes	Anal. (%) Found (Calcd) C	H	N	Mol. wt. Found	Calcd
1a	Ni(p-$CH_3OC_6H_4NC$)$_3$(TCNE)	61.42 (61.46	3.63 3.61	16.74 16.73)	626[a)]	586
1b	Ni(p-$CH_3C_6H_4NC$)$_3$(TCNE)	67.01 (66.93	3.77 3.94	18.26 18.22)	564[a)]	538
1c	Ni(C_6H_5NC)$_3$(TCNE)	65.44 (65.35	3.00 3.05	19.79 19.76)	524[a)]	496
1d	Ni(p-ClC_6H_4NC)$_3$(TCNE)	53 64 (54 09	2.28 2.02	15 33 16.36)	628[a)]	599
1e	Ni(2,4,6-$(CH_3)_3C_6H_2NC$)$_3$(TCNE)	69.64 (69.47	5.37 5.34	15.91 15.76)	602[b)]	622
2a	Co(NO)(p-$CH_3OC_6H_4NC$)$_2$(TCNE)	54.75 (54.67	2 94 2.92	20.00 20 54)	492[b)]	483
2b	Co(NO)(p-$CH_3C_6H_4NC$)$_2$(TCNE)	58 82 (58.55	3.18 3.13	21.76 21.72)	464[b)]	451
2c	Co(NO)(p-ClC_6H_4NC)$_2$(TCNE)	48.98 (48.81	1.62 1.64	19.63 19.93)	534[b)]	492
2d	Co(NO)(2,4,6-$(CH_3)_3C_6H_2NC$)$_2$(TCNE)	61.82 (61.54	4.36 4.37	19.13 19.33)	522[b)]	507

a,b) Measured by a vapor pressure osmometer in $CHCl_3$ at 25 °C (a) or in C_6H_6 at 37 °C (b).

Table 2. Relevant IR and PMR data of complexes

	Complexes	IR,[a)] cm^{-1} ν(NC)[b)]	ν(NO)	ν(CN)[c)]	PMR, δ(ppm)[f)] δ(–C_6H_n–)[g)]	$\delta(CH_3)$
	Ni(p-$CH_3OC_6H_4NC$)$_4$	2035 2010	—	—	7.12 6.98	3.79
1a	Ni(p-$CH_3OC_6H_4NC$)$_3$-(TCNE)	2166 2139	—	2215	7.48 6.91	3.81
1b	Ni(p-$CH_3C_6H_4NC$)$_3$-(TCNE)	2166 2137	—	2215	7.41 7.23	2.36
1c	Ni(C_6H_5NC)$_3$(TCNE)	2173[d)] 2142[d)]	—	2217[d)]	7.48s	—
1d	Ni(p-ClC_6H_4NC)$_3$-(TCNE)	2166 2135	—	2217	7.46s	—
	Ni(2,4,6-$(CH_3)_3$-C_6H_2NC)$_4$	— 2011	—	—	6 84s	2.36(o) 2.24(p)
1e	Ni(2,4,6-$(CH_3)_3C_6H_2$-NC)$_3$(TCNE)	2156 2122	—	2214	6.91s	2.42(o) 2.29(p)
	Co(NO)(p-CH_3OC_6-H_4NC)$_2$(CO)	2135 2091	1733	1985[e)]	7 36 6.90	3.82
2a	Co(NO)(p-CH_3OC_6-H_4NC)$_2$(TCNE)	2177 2161	1812	2219	7.56 6.99	3.86
2b	Co(NO)(p-$CH_3C_6H_4$-NC)$_2$(TCNE)	2174 2159	1813	2215	7.49 7.30	2 41
2c	Co(NO)(p-ClC_6H_4-NC)$_2$(TCNE)	2174 2157	1807	2217	7.55 7.47	—
2d	Co(NO)(2,4,6-$(CH_3)_3$-C_6H_2NC)$_2$(TCNE)	2173 2152	1810	2218	6.96s	2.45(o) 2.33(p)

a) Measured in C_6H_6 (0.03 M or less) unless otherwise noted. b) Isocyanide vibration. c) TCNE vibration. d) Measured in Nujol mulls. e) ν(CO). f) Measured in CH_2Cl_2 (0.04 M) at 25°C. g) A_2B_2-type quartet with a coupling constant of about 9 Hz unless otherwise noted; s=singlet.

The IR spectra of the TCNE complexes show a weak ν(CN) band around 2220 cm^{-1}, which indicates TCNE π-bonded through the C=C bond.[1,7] The ν(NC) frequency of the isocyanides is always higher in the TCNE complexes than in the starting complexes about 130 and 110 cm^{-1} (the differences between the averaged values of two frequencies) for the Ni and Co complexes respectively, indicating a charge transfer from the isocyanide ligands to the TCNE moiety. Moreover, in the Co series in Co(NO)(RNC)$_2$(TCNE) the ν(NO) bands shift to frequencies higher by about 80 cm^{-1} than those in Co(NO)(RNC)$_2$(CO). In the PMR spectra the isocyanide protons are always shifted to lower magnetic fields upon complex formation. These results indicate that TCNE is a stronger π-acid than carbon monoxide and isocyanides.

The electronic spectrum of Ni(p-$CH_3C_6H_4NC$)$_4$ shows an absorption maximum at 363 nm (ε 2.3×10^4); it is probably a charge transfer band from Ni to isocyanides. On the other hand, the corresponding band of **1b** may be blue-shifted and hidden under the strong band due to the isocyanide ligands. However, a new band appears at 452 nm (ε 2×10^3); its ε value suggests that this is a charge transfer band from Ni to TCNE. This is consistent with the stronger π-acceptor capacity of TCNE than those of isocyanides.

The IR spectrum of **1a** in C_6H_6 shows two strong ν(NC) bands of the isocyanides, indicating a C_{3v} local symmetry for the three isocyanides. The PMR spectrum in CH_2Cl_2 at 25 °C displays one sharp singlet and one A_2B_2-type quartet for the CH_3O and phenyl ring protons respectively; the magnetic equivalence of the three isocyanides is consistent with either the intramolecular rotation of TCNE (averaging the anisotropic effect of TCNE) or the rapid dissociative exchange of the ligands.

The molecular-weight determination reveals the essentially monomeric nature of **1a** (Table 1). The chemical shifts of the isocyanide protons were only slightly changed (0.02 ppm) when the concentration of **1a** in CH_2Cl_2 was changed from 0.20 to 0.008 M. The temperature dependence of the chemical shifts of **1a** in CH_2Cl_2 was found to be small (0.02 ppm) over the wide temperature range between −88 and 25 °C. These results suggest only a slight dissociation of ligands, if any. The addition of one molar equivalent of free TCNE to **1a** in CH_2Cl_2 at 25 °C did not affect the PMR spectrum; this eliminates the dissociative exchange of TCNE. On the other hand, the addition of three molar equivalents of free p-$CH_3OC_6H_4NC$ to **1a** in CH_2Cl_2 at 25 °C caused changes in the chemical-shift values; the isocyanide protons appeared at the averaged field between those of the complex and the free ligand. However, at −50 °C there occurred two sets of signals which exactly correspond to the complexed and free isocyanides, as is depicted in Fig. 1. This indicates a negligible dissociative exchange of isocyanides below −50 °C on the NMR time scale. However, no signal pattern indicative of the rotation being slowed down[3] was observed as low as −115 °C in a 1 : 4 mixture of CH_2Cl_2 and $CHClF_2$. This is also the case with the 2,4,6-$(CH_3)_3C_6H_2NC$ derivative, which is considered to be sterically most hindered. Thus, no direct evidence for the rotation being slowed down on the NMR time scale could be obtained. However, since the possibility of the rapid dissociative exchange of the ligands has been eliminated, the magnetic equivalence of the three isocyanides is more likely to be due to the free rotation of TCNE over a very low energy barrier.[8] Similar experiments were performed for some of the other Ni and Co complexes (**1b** and **2a**); the magnetic equivalence of the isocyanides observed for these complexes is also likely to be due to the free rotation of TCNE.

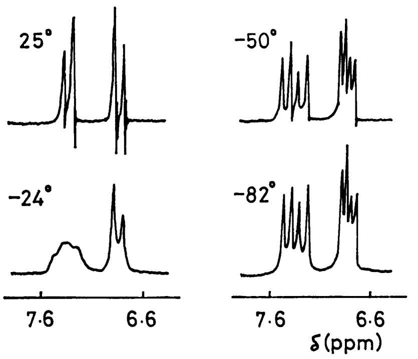

Fig. 1. Temperature-dependent PMR spectra of the phenyl ring protons of Ni(p-$CH_3OC_6H_4NC$)$_3$ (TCNE) (**1a**) in the presence of three molar equivalents of p-$CH_3OC_6H_4NC$ in CH_2Cl_2.

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8) The magnetic equivalence of the three t-C_4H_9NC in Ni(t-C_4H_9NC)$_3$(TCNE) was attributed to a slight dissociative exchange of the isocyanides without low-temperature PMR spectral measurements in the presence of free t-C_4H_9NC.[7]