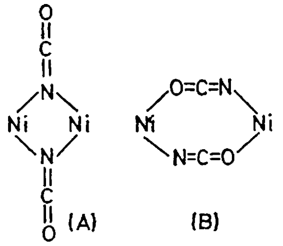
X-Ray Crystal Structure and Variable-temperature Magnetic Susceptibility of Di-μ-cyanato-bis-[2,2′,2″-triaminotriethylamine]dinickel(II) Tetraphenylborate; An Oxygen-bonded Cyanate

By D. Michael Duggan and David N. Hendrickson*

(*School of Chemical Sciences, University of Illinois, Urbana, Illinois* 61801)

Summary Variable-temperature (4·2—283 K) magnetic susceptibility and single-crystal *X*-ray crystallographic data are presented to demonstrate end-to-end di-μ-cyanate bridging in $[Ni_2(tren)_2(NCO)_2](BPh_4)$, where (tren) is $N(CH_2CH_2NH_2)_3$.

The cyanate ion (OCN^-) will in general co-ordinate to transition metals through the nitrogen atom.[1] Oxygen-bonded cyanates have only been claimed for complexes involving metals in high oxidation states (*e.g.*, Zr^{IV},[2] Pt^{IV},[3] Re^{IV},[4] Re^{V},[4] and Mo^{III}[4]), however, the existence of an oxygen-bonded complex has not to this date been unambiguously demonstrated. The cyanate anion has been found to bridge transition metals,[5–9] but the mode of bridging in each case is thought to be of a single-atom variety (mode A) rather than end-to-end (mode B).



We have prepared a complex which analyses to be $[Ni(tren)(NCO)](BPh_4)$, where tren is 2,2′,2″-triaminotriethylamine. In acetonitrile solution this material has an effective mol. wt. (4·065 mg ml^{-1} concentration) of 283, which is consistent with the presence of monomeric Ni(tren)(NCO)$^+$. In the solid state we have found that the cation is *dimeric* and thus the compound has the composition $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$. This nickel(II) dimer possesses mode B end-to-end cyanate bridging and as such is the first oxygen-bonded cyanate complex identified.

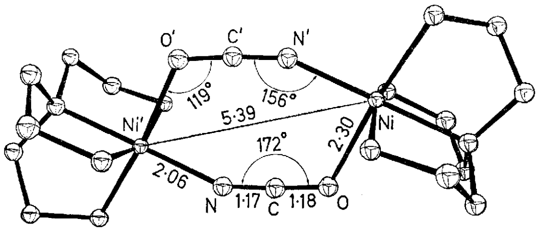


Figure. *ORTEP plotting of* $[Ni_2(tren)_2(NCO)_2]^{2+}$ *showing the geometrical parameters characterizing the di-μ-cyanate bridge.*

Two crystalline forms (as indicated by *X*-ray powder patterns) of $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$ have been found. One is formed directly from an aqueous solution of Ni^{2+}, (tren), and NCO^- upon precipitation with BPh_4^-, while the other results when the precipitated product is recrystallized from an acetonitrile solution. Variable-temperature (4·2—283 K) magnetic susceptibility data indicate that the same dimer cation is probably to be found in both crystalline forms. The μ_{eff} per nickel is relatively constant at 3·2 B.M. down to 200 K, whereupon it smoothly decreases to 0·85 B.M. at 4·2 K. A maximum in the susceptibility curve occurs at 14 K. Least-squares fitting to a theoretical expression[10] including an exchange term yielded the parameters: $J = -4·4$ cm^{-1}, $g = 2·28$, $D = 12·8$ cm^{-1}, where $2J$ is the energy separation between the $S' = 1$ and $S' = 0$ levels and D is the single-ion zero-field splitting. The acetonitrile-crystallized form exhibits identical magnetic properties.

The single crystal *X*-ray structure of acetonitrile-crystallized $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$ was solved with standard heavy atom Patterson and Fourier methods using 3077 observed reflections. The crystal system was determined to be monoclinic with $a = 32·360(18)$, $b = 10·650(7)$, $c = 19·319(14)$, and $\beta = 119·18(3)$. Flotation of crystals in a toluene-bromotoluene solution yielded $D_m = 1·297$ g cm^{-3}, whereas the unit cell parameters give ($M = 1132·4$, and $Z = 4$) $D_c = 1·294$. Refinement in the space group $C\,2/c$ with isotropic temperature factors on all dimer and tetraphenylborate atoms (hydrogen atoms were not included) yielded a weighted discrepancy factor of $R = 0·120$. The Figure shows an ORTEP[11] plotting of the model at this stage of refinement. The values of bond lengths and angles are tentative, pending further refinement. Possible errors are ±0·07 Å and 3°; only half of the geometry need be specified as the dimers lie on centres of symmetry. The atoms in the two cyanate bridges are almost co-planar (none deviating by more than 0·04 Å from a least squares plane fit to all six bridging atoms), while the nickel atoms lie above and below this plane by ±0·26 Å. All other dimer and tetraphenylborate dimensions are reasonable.

In a future paper we shall analyse and contrast the antiferromagnetic coupling observed for $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$ with the ferromagnetic coupling reported[10] for $[Ni_2(en)_4(NCS)_2]I_2$, which is a di-μ-thiocyanato-bridged dimer, also possessing mode (B) bridging.

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[11] ORTEP (ORNL-3794) was written by C. K. Johnson, Oak Ridge National Laboratories.

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