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Structural Characterization of an End-to-End Di-μ-cyanato-nickel Dimer. Di-μ-cyanato-bis(2,2',2''-triaminotriethylamine)dinickel(II) Tetraphenylborate

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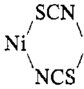
The structure of $[Ni_2(tren)_2(OCN)_2](BPh_4)_2$, where tren = 2,2',2''-triaminotriethylamine, has been determined using heavy-atom X-ray methods and refined by a full-matrix least-squares technique to an observed–calculated agreement of R_{wF} = 0.068 and R_F = 0.086 for 2624 observed reflections measured on a four-circle diffractometer. The molecule crystallizes in the $C2/c$ space group with 4 formula weights in a cell measuring a = 32.360 (18) Å, b = 10.650 (7) Å, c = 19.319 (14) Å, and β = 119.18 (3)°, with ρ_{obsd} = 1.30 g/cm³ and ρ_{calcd} = 1.29 g/cm³. Discrete cationic $[Ni_2(tren)_2(OCN)_2]^{2+}$ and anionic BPh_4^- units are found, where the metals are bridged by two cyanate groups bonding in an end-to-end mode. Each nickel atom in the cation is six-coordinate with tren occupying four sites (Ni–N = 2.047 (7), 2.054 (5), 2.095 (7), and 2.130 (7) Å) and with the other two sites of the distorted octahedron occupied by the N and O atoms of the bridging cyanate ions (Ni–N = 2.018 (7) Å and Ni–O = 2.336 (5) Å). The two cyanate bridges are essentially coplanar (largest deviation from the least-squares plane is ±0.008 Å) while the nickel atoms lie above and below the plane by ±0.25 Å and are separated from each other by 5.385 (1) Å. The bonding in the bridging unit (C–N = 1.128 (10) Å and C–O = 1.220 (10) Å in OCN^-) is discussed. In addition, the conformation and inter-ring interactions of the tetraphenylborate anion are discussed. Nuclear repulsion calculations indicate that the BPh_4^- anion is in an energetically favorable conformation and as such it is probable that the favorable packing of the $[Ni_2(tren)_2NCO)_2]^{2+}$ cation and the BPh_4^- anions leads to the isolation of a salt of this unique dimeric unit.

Introduction

The existence of an oxygen-bonded cyanate complex has been an oft-debated issue for many years.[2] Although end-to-end bridged cyanates[3] and M–OCN terminally bound cyanates[4,5] have been claimed, in no case has such a report been substantiated. Contrary to the situation with the thiocyanate (SCN^-) and selenocyanate ($SeCN^-$) ions, which apparently have been more thoroughly studied, the cyanate ion bonds in most circumstances only with its nitrogen atom, this ostensibly being due[5] to the small charge density on the cyanate oxygen atom compared to that associated with the cyanate nitrogen. Molecular orbital calculations, however, have *not* indicated a disparity in net electron density between the cyanate nitrogen or oxygen.[6] The belief in a relatively low cyanate–oxygen electron density and the fact that oxygen-bound complexes had been claimed for only highly charged metal ions (*e.g.*, Pt(IV),[5] Re(IV),[3] Re(V),[3] Mo(III),[3] and Ti(IV)[4]) led to the belief that a metal–OCN interaction requires a metal center with a low electron density, either through being highly oxidized or by having strong "π-acceptor" ligands.

In light of the above it was of interest that we were able to prepare a Ni(II) compound that by virture of its antiferromagnetic exchange properties[7,8] was known to be dimeric with the formulation $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$, where tren is 2,2',2''-triaminotriethylamine. As a result of a comparison of the X-ray powder pattern for this compound with that for the μ-oxalato compound $[Ni_2(tren)_2C_2O_4)](BPh_4)_2$,[9] it was our contention that the former possessed

bridging. This led to an investigation of the cyanate compound with single-crystal X-ray techniques. A demonstration of such dicyanate bridging would provide the first authenticated case of metal–OCN bonding and initiate a proper focus on the metal center's requisites in such an interaction. Our interest in the structure of $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$, which exhibits an *antiferromagnetic* exchange interaction, also lies in a comparison of the geometry of the di-μ-cyanate bridge with that of the closely related



bridge found[10] in $[Ni_2(en)_4(NCS)_2]I_2$, a compound which exhibits a ferromagnetic exchange interaction.[11]

Experimental Section

Compound Preparation. Samples of $[Ni_2(tren)_2(NCO)_2](BPh_4)_2$ were prepared by dissolving 0.01 mol of $NiSO_4 \cdot 6H_2O$ and 0.01 mol of NaOCN in 300 ml of distilled water, to which was first added 1.5 ml of tren (obtained from Ames Laboratories) and then with stirring ~0.5 g of $NaBPh_4$ in 50 ml of H_2O. The resulting precipitate was filtered and washed with water and diethyl ether and dried *in vacuo* over P_2O_5.

Crystals suitable for X-ray work were prepared from this powder by dissolution and slow evaporation from acetonitrile. It was found by X-ray powder pattern studies that the powder and crystallized materials have different crystal structures. However, ir and variable-temperature magnetic susceptibility data showed[7] that the $[Ni_2(tren)_2(NCO)_2]^{2+}$ dimer unit is the same in each case.

Crystal Measurements. X-Ray work was carried out at 25° on a rectangular prismatic blue-violet crystal of dimensions 0.42 mm × 0.21 mm × 0.19 mm, which was mounted perpendicular to the 0.42 × 0.21 mm face, corresponding to the a^* axis of the reciprocal-space unit cell. The crystal system was determined to be monoclinic with a = 32.360 (18) Å, b = 10.650 (7) Å, c = 19.319 (14) Å, and β = 119.18 (3)°. Flotation of three crystals in a toluene–bromotoluene mixture yielded ρ_{measd} = 1.30 g/cm³, whereas that determined from

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[1] Esso Fellow, 1971–1972; Mobil Fellow, 1972–1973.

[2] A. H. Norbury and A. I. P. Sinha, *Quart. Rev.* (*London*), 24, 69 (1970).

[3] R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, 31, 689 (1969).

[4] J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, 8, 170 (1969).

[5] J. Powell and B. L. Shaw, *J. Chem. Soc.* 3879 (1965).

[6] F. J. Hasboer and W. Beck, *Chem. Commun.*, 262 (1970).

[7] D. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 411 (1973).

[8] D. M. Duggan and D. N. Hendrickson, submitted for publication.

[9] D. M. Duggan and D. N. Hendrickson, unpublished results.

[10] A. F. Shvelashvili, M. A. Porai-Koshits, and A. S. Antsyshkina, *J. Struct. Chem.* (*USSR*), 10, 552 (1969).

[11] A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, 11, 2884 (1972).

the unit cell parameters (mol wt 1132, $Z = 4$) was $\rho_{\text{calcd}} = 1.29$. The systematic absences were found to be hkl when $h + k = 2n + 1$ and $h0l$ when $l = 2n + 1$ (by precession photography) which are consistent with either of the space groups Cc or $C2/c$.

Previous to data collection, 10 hand-centered reflections were used to calculate accurate unit cell parameters by least-squares fitting using a computer-controlled four-circle Picker diffractometer. The values obtained are $a = 32.360$ (18) Å, $b = 10.650$ (7) Å, $c = 19.319$ (14) Å, and $\beta = 119.18$ (3)°.

Data were collected from $2\theta = 3°$ to $2\theta = 45°$ using Mo Kα radiation monochromated by a graphite crystal set at a takeoff angle of 1.32°. The θ–2θ scan technique was used, where the base width was set to 2° in 2θ and the scans were made at 1°/min. Dispersion corrections were made to account for the separation of Mo Kα_1 and Mo Kα_2 at high angles. Background counts were made for 10 sec on each side of the peak. Three standard reflections in diverse regions of crystal space were collected after every 50 reflections measured. Two of these remained above 98% of their initial intensity values throughout data collection, while the third fell to 96%. No correction was made for these deviations as in our estimation they are not serious. There were 3953 independent reflections measured, of which 3077 were observed at the 1σ level $\{I_{\text{obsd}} > 1\sigma(I)$ where $\sigma(I) = [T_{\text{c}} + (t_{\text{c}}/t_{\text{b}})^2(B_1 + B_2)]^{1/2}$, T_{c} is the total integrated peak count, $t_{\text{c}}/t_{\text{b}}$ is the ratio of time spent counting the peak intensity to the time of counting the background, and B_1 and B_2 are the background counts$\}$, while 2624 were observed at the 2σ level. Lorentz and polarization corrections were applied to the data at the start of the calculations. Standard deviations were assigned to the structure factors on the basis of counting statistics; $\sigma(|F|) = (|F|/2I)[T_{\text{c}} + 0.25 \cdot (t_{\text{c}}/t_{\text{b}})^2(B_1 + B_2) + (0.02I)^2]^{1/2}$.

Structure Solution and Refinement

All structure calculations described below were performed using spherical atom scattering factors taken from the compilations of Hansen, *et al.*[12] (Ni(II), N, B, H) and Cromer and Mann[13] (C). Because refinement proceeded smoothly in the space group $C2/c$, no attempt was made to disprove the Cc space group possibility by R factor tests. Anomalous scattering was accounted for in the scattering factors of the nickel atom. The magnitudes of $\Delta f'$ and $\Delta f''$ were obtained from "International Tables for X-Ray Crystallography."

Calculating a Patterson function (using all reflections observed at the 1σ level) enabled the accurate location of the nickel atoms and showed them to be paired about centers of symmetry at the ($^1/_4$, $^1/_4$, 0) and ($^3/_4$, $^1/_4$, $^1/_2$) special positions. The nickel atom position was used initially to phase the Fourier calculations, two of which gave the location of the OCN bridging atoms and all tetraphenylborate atoms. A difference Fourier, at this point, showed all atoms of the tren ligand.

Isotropic least-squares refinement of all 39 nonhydrogen atoms was carried out minimizing $\Sigma w||F_{\text{o}}| - |F_{\text{c}}||^2$, where $w = 1/(\sigma(F))^2$, using the program ORFLS (Busing and Levy). After three cycles the weighted R factor $R_{\text{w}F} = (\Sigma w|F_{\text{o}} - F_{\text{c}}|^2/\Sigma wF_{\text{o}}^2)^{1/2}$, was 0.117 (unobserved reflections were given weights of zero). Because there are too many parameters for simultaneous refinement of both dimer and tetraphenylborate atoms using anisotropic temperature factors (program limit = 270 variables), further refinement was carried out in segments. Variation of all dimer parameters including anisotropic temperature factors converged after two iterations at $R_{\text{w}F} = 0.105$. Fixing the dimer parameters and assigning anisotropic parameters to all 25 of the BPh_4^- atoms resulted, after two additional cycles, in $R_{\text{w}F} = 0.096$.

Table I. Positional Parameters for All Atoms of the Dimeric Cation $[\text{Ni}_2(\text{tren})_2(\text{OCN})_2]^{2+}$, Including Isotropic Temperature Factors for the Hydrogens[a]

Atom	x	y	z	B, Å^2
Ni	0.82235 (3)	0.15712 (9)	0.48420 (5)	
N1	0.8783 (2)	0.0235 (5)	0.5353 (3)	
N2	0.8672 (2)	0.2692 (5)	0.5765 (3)	
N3	0.8495 (2)	0.1870 (5)	0.4092 (3)	
N4	0.7840 (2)	−0.0051 (6)	0.4280 (3)	
N5	0.7670 (2)	0.2765 (5)	0.4336 (3)	
C1	0.9103 (3)	0.0676 (7)	0.6159 (5)	
C2	0.9156 (3)	0.2098 (8)	0.6148 (4)	
C3	0.9029 (2)	0.0117 (7)	0.4865 (5)	
C4	0.8719 (3)	0.0669 (7)	0.4040 (5)	
C5	0.8571 (3)	−0.0954 (7)	0.5387 (5)	
C6	0.8159 (3)	−0.1210 (7)	0.4571 (5)	
C7	0.7621 (2)	0.1627 (7)	0.5683 (4)	
O	0.7941 (2)	0.0996 (4)	0.5702 (3)	
H1	0.856	0.276	0.616	3.9
H2	0.869	0.353	0.557	3.9
H3	0.935	0.239	0.670	5.0
H4	0.932	0.230	0.585	5.0
H5	0.897	0.045	0.651	4.1
H6	0.942	0.026	0.636	4.1
H7	0.874	0.254	0.431	4.0
H8	0.824	0.211	0.356	4.0
H9	0.892	0.083	0.379	4.1
H10	0.847	0.005	0.372	4.1
H11	0.933	0.058	0.513	4.2
H12	0.909	−0.078	0.481	4.2
H13	0.771	0.003	0.370	4.3
H14	0.758	−0.015	0.440	4.3
H15	0.828	−0.140	0.420	5.4
H16	0.797	−0.193	0.460	5.4
H17	0.881	−0.164	0.554	4.6
H18	0.846	−0.090	0.578	4.6

[a] Estimated standard deviations in parentheses.

Hydrogen atoms were added to the model at this time. Because the positions of all 34 of the hydrogen atoms were not clearly indicated on a difference Fourier, they were generated using the program HYGEN.[14] In this procedure it was assumed that all carbon and nitrogen atoms in the tren ligand are sp^3 hybridized, while the benzene moieties possessed trigonal hybridization. The validity of these assumptions was verified by the bond angles at this point, angles which were mostly within 4° of tetrahedral and trigonal, respectively. Carbon–hydrogen and nitrogen–hydrogen distances were all taken as 0.99 Å. The temperature factors used for the hydrogen atoms (not varied) were those of the atoms to which they are attached as calculated from the isotropically refined model. After two more cycles varying the parameters of the dimer and then four more for the BPh_4^-, the $R_{\text{w}F}$ factor was 0.074. Here two of the largest reflections $[(\overline{12},0,0)$ and $(\overline{6}02)]$ with $2\theta < 15°$, which appeared to be affected by extinction ($F_{\text{o}} \leqslant 0.90F_{\text{c}}$), were removed from the data set.

Final refinement was performed both with all 3951 reflections in the data set (two removed as stated above) and with the smaller 2622 reflection 2σ cutoff data set. For the larger data set the final $R_{\text{w}F}$ was 0.072, while $R_F = \Sigma(|F_{\text{o}}| - |F_{\text{c}}|)/|F_{\text{o}}|$ was 0.137, and the estimated standard deviation of an observation of unit weight (ERF) calculated from $[\Sigma w(F_{\text{o}} - F_{\text{c}})^2/(\text{NO} - \text{NV})]^{1/2}$, where NO is the number of observables and NV is the number of variables, is 4.13. Using the smaller data set gave $R_{\text{w}F} = 0.068$, $R_F = 0.086$, and ERF = 4.85. As there are no significant differences in bond lengths for calculations from the two data sets, only results for the former are reported, because refinement using all observed and unobserved data is a generally accepted procedure. It was thought that the relatively high ERF values could be due to systematic errors resulting from absorption for which we did not correct. When an absorption correction was made and the structure refined to convergence, the R factors were only slightly decreased, the ERF for the larger data set was reduced to 4.02, and no bond lengths changed by a statistically meaningful amount.

A check was made of the assumed identities of the oxygen and nitrogen cyanate atoms. This was done in two ways. First, both atoms were removed from the anisotropically refined model and a difference Fourier was calculated which revealed peaks at the assumed oxygen and nitrogen positions of 8.10 and 6.85 e/Å^3, respectively. Second, the scattering factors for the two atoms were exchanged and one cycle of least-squares refinement was calculated. The temperature factors of the nitrogen were observed to increase while those of the oxygen decreased. For both atoms B_{11}, B_{22}, and B_{33} changed by more than half of the original values. Both the removal and switching calculations indicate that the atoms are assigned correctly.

The final difference map for this structure showed no peaks or holes greater than 1 e/Å^3 in any region. The largest parameter shift for the last cycle was less than half of the estimated error in that parameter.

It should be noted that there were large shifts of the N–C and C–O cyanate dimensions during the refinement. The final dimen-

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(12) H. P. Hansen, F. Herman, J. O. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(13) D. T. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(14) F. K. Ross, Doctoral Dissertation, University of Illinois, 1969.

Table II. Temperature Factors and Estimated Standard Deviations for the $[Ni_2(tren)_2(OCN)_2]^{2+}$ Cation,[a] $\times 10^4$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	9.7 (2)	58.5 (11)	32.9 (5)	3.8 (4)	9.9 (2)	3.5 (7)
N1	9 (1)	48 (8)	31 (3)	7 (2)	3 (2)	1 (4)
N2	18 (1)	57 (7)	40 (3)	3 (3)	13 (2)	1 (4)
N3	16 (1)	115 (9)	28 (3)	−8 (3)	12 (2)	10 (4)
N4	9 (1)	91 (8)	47 (3)	−13 (3)	4 (2)	−9 (5)
N5	6 (1)	107 (9)	42 (3)	16 (2)	10 (2)	28 (4)
C1	20 (2)	44 (10)	46 (5)	−8 (3)	11 (2)	6 (6)
C2	14 (2)	152 (14)	25 (4)	−14 (4)	6 (2)	−16 (6)
C3	15 (2)	133 (12)	38 (5)	1 (4)	11 (2)	4 (6)
C4	20 (2)	113 (13)	59 (5)	9 (4)	26 (3)	−11 (7)
C5	17 (2)	60 (10)	59 (5)	−13 (3)	10 (3)	7 (6)
C6	20 (2)	88 (12)	65 (6)	−21 (4)	6 (3)	8 (7)
C7	8 (2)	80 (12)	34 (4)	26 (3)	8 (2)	3 (6)
O	13 (1)	92 (7)	40 (3)	16 (2)	15 (1)	18 (4)

[a] The form of the anisotropic thermal elipsoid is given by exp$[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

sions reported in this paper are different from those communicated[7] earlier after only isotropic refinement. These differences were unexpected and seem to be due to strong correlation of the bridge parameters with those of the tetraphenylborate ion. It was noticed that the observed 0.04-Å shift in cyanate dimensions occurred only after careful refinement of the BPh_4^- ion with hydrogen atoms. The *positional* parameters of *both* the cation and the anion were refined together and a correlation matrix was calculated which showed all interion correlations were less than ~0.05 with the exception of those for boron-oxygen and boron-C7 which were found to be as large as 0.45 in confirmation of the empirically observed coupling.

The final values h, k, l, $|F_o|$, and $|F_c|$ will appear in the microfilm edition of the journal.

Discussion

Discrete $[Ni_2(tren)_2(OCN)_2]^{2+}$ and BPh_4^- entities are found in the solid-state structure of the material whose empirical composition is [Ni(tren)OCN]BPh_4. In Tables I and II are given the final positional parameters and temperature factors for the dimeric cation $[Ni_2(tren)_2(OCN)_2]^{2+}$. The most outstanding feature of the dimer is evident in Figure 1. The two nickel(II) atoms are bridged by two cyanate ions (OCN^-) in an end-to-end fashion. Each cyanate ion bonds to the nickel atoms with *both* its nitrogen and oxygen atoms. This, then, is the *first* authenticated oxygen-bonded metal cyanate complex.

It was of interest (particularly with respect to the magnetic susceptibility studies[7,8]) to note the actual stereochemistry of the nickel atoms and the orientation of the nickel coordination spheres relative to the bridge. As Figure 1 illustrates, the nickel atoms are octahedrally coordinated with the tren Ni-N distances ranging from 2.047 (7) to 2.130 (7) Å, while the Ni-N(NCO) and Ni-O(NCO) distances are shorter (2.018 (7) Å) and longer (2.336 (5) Å), respectively. A compilation of bond distances and angles for $[Ni_2(tren)_2(OCN)_2]^{2+}$ is given in Table III. The NiNC, NCC, and CNC angles in the Ni(tren) system are all close to 109°, indicating an essentially unstrained tren ligand. The two cyanate bridges are coplanar, the largest deviation from the least-squares plane being ±0.008 Å. The nickel atoms lie out of the plane by ±0.25 Å and are separated from each other by 5.385 (1) Å. The least-squares plane including the atoms Ni, N1, N3, N5, and O (see Figure 1 for labeling) makes an angle of 7.07° with the plane through the six atoms of the bridging groups.

Table III. Bonding Distances (A) and Angles (deg) for the $[Ni_2(tren)_2(OCN)_2]^{2+}$ Cation with Estimated Standard Deviations Given in Parentheses[a]

Distances			
Ni-N1	2.130 (7)	N1-C3	1.507 (11)
Ni-N2	2.047 (7)	N3-C4	1.497 (10)
Ni-N3	2.054 (5)	C3-C4	1.527 (13)
Ni-N4	2.095 (7)	N1-C5	1.457 (10)
Ni-N5	2.018 (7)	N4-C6	1.529 (10)
Ni-O	2.336 (5)	C5-C6	1.515 (13)
N1-C1	1.466 (11)	C7-O	1.220 (9)
N2-C2	1.506 (10)	N5-C7′	1.128 (10)
C1-C2	1.525 (11)	Ni-Ni′	5.385 (1)
Angles			
N1-Ni-N2	84.5 (2)	Ni-N1-C5	106.8 (3)
N1-Ni-N3	82.6 (2)	C1-N1-C3	112.2 (5)
N1-Ni-N4	81.0 (2)	C1-N1-C5	109.5 (7)
N1-Ni-N5	177.1 (2)	C3-N1-C5	111.1 (6)
N1-Ni-O	92.0 (2)	Ni-N2-C2	108.0 (4)
N2-Ni-N3	99.1 (2)	Ni-N3-C4	107.6 (4)
N2-Ni-N4	157.2 (2)	Ni-N4-C6	110.7 (5)
N2-Ni-N5	98.1 (2)	Ni-C1-C2	109.2 (7)
N2-Ni-O	83.7 (2)	N2-C2-C1	109.1 (7)
N3-Ni-N4	96.3 (2)	N1-C3-C4	110.0 (7)
N3-Ni-N5	98.3 (2)	N3-C4-C3	110.6 (7)
N3-Ni-O	173.5 (2)	N1-C5-C6	107.7 (5)
N4-Ni-N5	96.1 (2)	N4-C6-C5	109.4 (8)
N4-Ni-O	79.3 (2)	Ni-O-C7	117.1 (5)
N5-Ni-O	87.0 (2)	Ni-N5-C7′	155.0 (6)
Ni-N1-C1	106.2 (4)	O-C7-N5′	178.5 (9)
Ni-N1-C3	110.8 (5)		

[a] Primed atoms related to those given by the transformation: $1^1/_2 - x$, $^1/_2 - y$, $1 - z$.

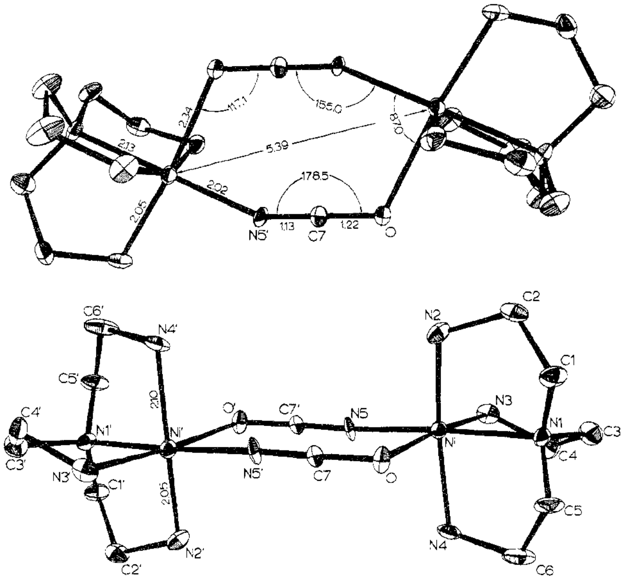

Figure 1. ORTEP plotting of $[Ni_2(tren)_2(OCN)_2]^{2+}$ showing some important geometrical parameters characterizing the di-μ-cyanate bridge and the nickel coordination environment. Hydrogen atoms are not shown.

The Ni-N(OCN) distance of 2.018 (7) Å is certainly well within the range established for Ni-N bonds, although the Ni-O(OCN) distance of 2.336 (5) Å seems to be somewhat long in comparison to other Ni-O bond lengths. For instance, the Ni-O distance in bis(acetylacetonato)nickel(II) has been determined[15] to be 1.90 Å, which is to be compared with 1.84 Å for Ni-O in bis(salicylideniminato)nickel(II).[16] The Ni-O(OCN) distance in $[Ni_2(tren)_2(OCN)_2]^{2+}$ is also appreciably larger than a Ni-O distance (~2.0 Å) for coordination of water to nickel.[17] Nevertheless, in view of the magnetic interaction[7,8] of the two nickel atoms and the en-

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(15) S. Shibata, M. Kishita, and M. Kubo, *Nature (London)*, 179, 320 (1957); S. Shibata, *Bull. Chem. Soc. Jap.*, 30, 753 (1957).

(16) J. M. Stewart and E. C. Lingafelter, *Acta Crystallogr.*, 12, 842 (1959).

(17) D. M. Liebig, J. H. Robertson, and M. R. Truter, *J. Chem. Soc. A*, 879 (1966).

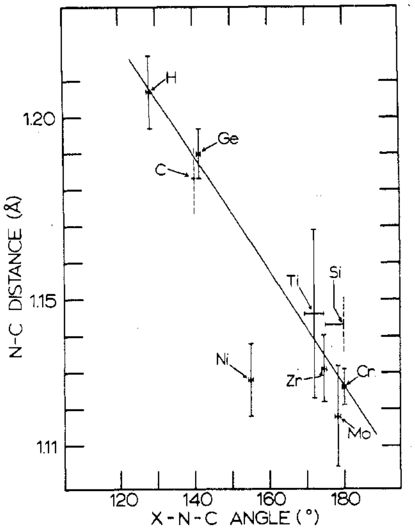
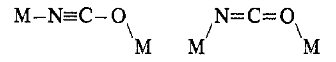


Figure 2. Plot of C-N bond distance *vs.* MNC bond angle for a series of terminally N-bonded cyanate complexes. Approximate error bars are indicated and dashed lines are used when no error values were reported. Labels identify the X group of the molecules listed in Table IV.

forced octahedral geometry about each metal, it is clear that the Ni-O(OCN) distance in this case is representative of an energetically important and indeed *bonding* interaction. Further comments are made on this matter later in this section.

It is relevant to note that the cyanate carbon-oxygen and carbon-nitrogen distances are similar to those found[18-20] in terminally N-bonded transition metal systems. Table IV lists the cyanate dimensions of other structurally characterized cyanate-containing molecules. These terminally N-bonded systems fall into two groups based on their MNC angles and N-C distances, as illustrated by a plot of ∠MNC *vs.* d_{NC} shown in Figure 2. This group distinction points out that for those molecules where the MNC angle approaches 120° the C-N distance tends toward what would be expected for a C=N double bond; on the other hand, when the MNC angle approaches 180°, the C-N distance is short, indicative of a C≡N triple bond. All of the terminally bound *transition* metal cyanate systems investigated to date fall in this latter category. It is curious then that the C-N distance in $[Ni_2(tren)_2(OCN)_2](BPh_4)_2$ is reminiscent of a triple-bonded C≡N pair, while the MNC angle deviates from linearity by some 25° (note the position of this compound on the graph in Figure 2). It is also notable that the MOC angle is significantly larger than 109° and approaches 120°, the sp^2 bonding angle. The angular considerations, taken together, seem to indicate that the cyanate bonding in this case may be described by a combination of the "resonance" forms



$$\mathrm{M{-}N{\equiv}C{-}O{\diagdown}M} \qquad \mathrm{M{\diagup}N{=}C{=}O{\diagdown}M}$$

A B

The average bond angles for these two forms are MNC ≃ 150° and MOC ≃ 115°, which are reasonably close to those found. This description can only be taken as pictorially convenient, however, for as noted above the shortness of the C-N distance strongly supports form A only. Apparently, adding a second metal to what otherwise would be a linear M-NCO system allows a fairly large and energetically favorable bending of the MNC bond but changes in the NC bond length that are immeasurably small, due to the large amount of energy associated with this bond.

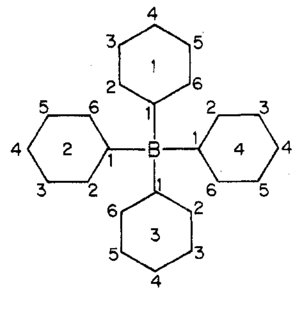
Table IV. Dimensions for Terminally N-Bonded Cyanate

Molecule	N-C, Å	C-O, Å	XNL, deg	Ref
HNCO	1.207 (10)	1.170 (10)	128.1	*a*
H_3CNCO	1.19 (3)	1.18 (3)	125,[b] 140[c]	
H_3SiNCO	1.150	1.179	~180	*d*
H_3GeNCO	1.190 (7)	1.182 (7)	141.3 (4)	*e*
$Cp_2Ti(NCO)_2$	1.146 (23)	1.210 (22)	172.0 (27)	*f, i*
$CpCr(NO_2)(NCO)$	1.126 (5)	1.179 (6)	180.0 (4)	*g*
$CpMo(CO)(PPh_3)_2$-(NCO)	1.118 (14)	1.238 (16)	178.3 (9)	*h*
$Cp_2Zr(NCO)_2$	1.131 (9)	1.178 (9)	174.5 (5)	*f, i*
$[Ni_2tren_2(OCN)_2]$-$(BPh_4)_2$	1.128 (10)	1.220 (9)	155.0 (6)	*j*

[a] L. H. Jones, J. N. Shoolery, R. G. Shulman, and D. M. Yost, *J. Chem. Phys.*, 18, 990 (1950). [b] E. H. Eystor, R. H. Gillette, and L. O. Brockway, *J. Amer. Chem. Soc.*, 62, 3236 (1940). [c] R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *J. Chem. Phys.*, 39, 3355 (1963). [d] M. C. L. Gerry, J. C. Thompson, and T. M. Sugden, *Nature (London)*, 211, 846 (1966). [e] J. D. Murdoch and D. W. H. Rankin, *J. Chem. Soc., Chem. Commun.*, 748 (1972). [f] A. A. Kossiakoff, R. H. Wood, and J. L. Burmeister, submitted for publication. [g] M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 605 (1970). [h] A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *ibid.*, 205 (1971). [i] Average of both cyanates. [j] This work.

Infrared data also serve to illustrate the predominantly N-bonded characteristic of the cyanate bridging. The asymmetric cyanate stretching vibration (ν_a) in $[Ni_2(tren)_2(OCN)_2](BPh_4)_2$ is at 2217 cm^{-1}, which is quite normal for ostensibly triple-bonded forms, while the symmetric stretching vibration (ν_s) is at 1299 cm^{-1}, which is also normal for terminally N-bonded cyanates, although much higher than *expected*[2,4] for O-bonded cyanates. Low-energy (~1100-1250 cm^{-1}) ν_s bands have been reported in the literature[3,4] for systems potentially involving M-OCN bonding. However, the position of the ν_s vibration in our system where M-OCN bonding *is* involved and the recent X-ray investigation[21] of two systems, $[Ti(\pi\text{-}C_5H_5)_2(NCO)_2]$ and $[Zr(\pi\text{-}C_5H_5)_2(NCO)_2]$, with reported low-energy ν_s bands where M-OCN is *not* involved call for considerable caution when using ir criteria for identifying the bonding mode of the cyanate ion. This is particularly true when the *proposed* formulation is a bridging one or when the assignment of the ν_s band is less than certain.

In light of the recent[21] structural review of the tetraphenylborate anion, it is interesting to examine the BPh_4^- structure found in this study. In Tables V and VI are given the positional parameters and temperature factors for the tetraphenylborate ion, where the labeling scheme is



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(18) A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc. A*, 205 (1971).

(19) M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 605 (1970).

(20) A. A. Kossiakoff, R. H. Wood, and J. L. Burmeister, submitted for publication in *Inorg. Chem.*

(21) M. Di Vaira and A. B. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972).

Table V. Positional Parameters for All Atoms of the Anion $B(C_6H_5)_4^-$, Including Isotropic Temperature Factors for the Hydrogens[a]

Atom	x	y	z	B, Å^2
B	0.6152 (3)	0.9395 (9)	0.2565 (5)	
C11	0.5739 (2)	0.8464 (8)	0.1862 (5)	
C12	0.5584 (3)	0.8763 (7)	0.1061 (6)	
C13	0.5251 (3)	0.7951 (10)	0.0442 (4)	
C14	0.5093 (4)	0.6931 (9)	0.0620 (8)	
C15	0.5219 (4)	0.6640 (10)	0.1365 (6)	
C16	0.5544 (3)	0.7392 (8)	0.1987 (5)	
C21	0.6143 (3)	0.9224 (6)	0.3403 (5)	
C22	0.5727 (3)	0.9203 (7)	0.3445 (5)	
C23	0.5701 (3)	0.9198 (8)	0.4138 (6)	
C24	0.6109 (4)	0.9250 (8)	0.4856 (6)	
C25	0.6538 (3)	0.9298 (7)	0.4868 (5)	
C26	0.6551 (3)	0.9279 (6)	0.4152 (5)	
C31	0.6646 (3)	0.8774 (7)	0.2645 (4)	
C32	0.6825 (3)	0.7581 (8)	0.3032 (4)	
C33	0.7222 (3)	0.6979 (8)	0.3050 (5)	
C34	0.7471 (3)	0.7568 (10)	0.2712 (6)	
C35	0.7312 (3)	0.8687 (8)	0.2344 (5)	
C36	0.6908 (3)	0.9298 (7)	0.2304 (4)	
C41	0.6095 (3)	1.0893 (7)	0.2352 (4)	
C42	0.6464 (3)	1.1733 (7)	0.2615 (5)	
C43	0.6397 (3)	1.2973 (8)	0.2448 (5)	
C44	0.5952 (3)	1.3469 (7)	0.2009 (5)	
C45	0.5593 (3)	1.2681 (9)	0.1747 (5)	
C46	0.5645 (2)	1.1392 (8)	0.1908 (4)	
H(12)	0.570	0.953	0.093	4.1
H(13)	0.514	0.817	−0.012	4.7
H(14)	0.488	0.636	0.019	4.6
H(15)	0.508	0.589	0.148	4.2
H(16)	0.564	0.714	0.254	4.2
H(22)	0.543	0.919	0.294	4.7
H(23)	0.539	0.916	0.412	3.9
H(24)	0.609	0.925	0.536	5.1
H(25)	0.684	0.934	0.538	5.3
H(26)	0.686	0.931	0.418	3.0
H(32)	0.667	0.717	0.330	3.4
H(33)	0.732	0.614	0.330	4.1
H(34)	0.776	0.717	0.275	4.4
H(35)	0.748	0.909	0.209	4.8
H(36)	0.681	1.012	0.203	4.0
H(42)	0.679	1.142	0.294	3.8
H(43)	0.668	1.354	0.265	3.3
H(44)	0.590	1.438	0.190	4.0
H(45)	0.527	1.302	0.142	4.4
H(46)	0.536	1.084	0.171	3.4

[a] Estimated standard deviations in parentheses.

Table VI. Temperature Factors and Estimated Standard Deviations for the Tetraphenylborate Anion,[a] ×10⁴

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
B	5 (2)	122 (15)	35 (5)	4 (4)	7 (2)	−6 (7)
C11	6 (1)	77 (11)	34 (4)	9 (3)	7 (2)	−3 (6)
C12	9 (14)	99 (12)	48 (5)	5 (3)	14 (2)	8 (7)
C13	9 (2)	237 (17)	14 (4)	12 (4)	1 (2)	−40 (7)
C14	29 (3)	63 (14)	185 (12)	−36 (5)	66 (5)	−72 (11)
C15	25 (2)	113 (14)	83 (8)	−16 (4)	33 (4)	4 (9)
C16	12 (2)	59 (11)	55 (5)	−13 (3)	11 (2)	−11 (6)
C21	11 (1)	29 (9)	36 (4)	4 (3)	13 (2)	3 (5)
C22	11 (1)	79 (10)	40 (5)	8 (3)	12 (2)	8 (6)
C23	15 (2)	120 (13)	57 (6)	6 (4)	16 (3)	11 (8)
C24	26 (2)	67 (11)	71 (6)	9 (5)	34 (3)	−6 (7)
C25	18 (2)	45 (10)	27 (4)	8 (4)	5 (2)	−4 (5)
C26	10 (1)	54 (10)	37 (4)	0 (3)	14 (2)	−2 (6)
C31	11 (1)	61 (11)	14 (4)	−7 (3)	2 (2)	−16 (5)
C32	13 (2)	87 (11)	27 (4)	−8 (3)	10 (2)	−5 (6)
C33	17 (2)	80 (12)	34 (5)	21 (4)	4 (2)	−14 (6)
C34	13 (2)	138 (2)	63 (6)	1 (4)	16 (3)	−21 (8)
C35	16 (2)	75 (12)	46 (5)	−9 (4)	14 (3)	−19 (6)
C36	11 (14)	96 (11)	30 (4)	−6 (3)	10 (2)	−5 (5)
C41	12 (2)	52 (10)	25 (4)	12 (3)	12 (2)	14 (5)
C42	11 (1)	53 (10)	44 (5)	−6 (3)	−14 (2)	−3 (6)
C43	13 (2)	61 (12)	54 (5)	−3 (4)	13 (3)	−2 (6)
C44	18 (2)	42 (10)	63 (6)	−12 (4)	21 (3)	−5 (6)
C45	16 (2)	89 (12)	38 (5)	24 (4)	10 (2)	24 (7)
C46	7 (1)	107 (12)	29 (4)	−6 (3)	7 (2)	−10 (6)

[a] The form of the anisotropic thermal elipsoid is given by exp$[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table VII. Bonding Distances (Å) and Angles (deg) for the Tetraphenylborate Anion, with Estimated Standard Deviations

Distances

B–C11	1.687 (13)	B–C31	1.667 (13)
C12–C11	1.410 (14)	C31–C36	1.417 (12)
C12–C13	1.443 (13)	C35–C36	1.429 (13)
C11–C16	1.382 (12)	C31–C32	1.444 (11)
C13–C14	1.317 (15)	C35–C34	1.354 (14)
C16–C15	1.400 (15)	C32–C33	1.420 (13)
C14–C15	1.327 (20)	C34–C33	1.409 (14)
C22–C23	1.381 (15)	B–C41	1.635 (13)
B–C21	1.644 (14)	C41–C46	1.386 (12)
C22–C21	1.389 (13)	C41–C42	1.376 (12)
C23–C24	1.372 (16)	C46–C45	1.400 (13)
C21–C26	1.407 (13)	C42–C43	1.353 (12)
C24–C25	1.381 (15)	C45–C44	1.319 (13)
C26–C25	1.403 (13)	C43–C44	1.371 (14)

Angles

C11–B–C21	109.9 (8)	C23–C24–C25	118.8 (6)
C11–B–C31	100.9 (4)	C21–C26–C25	123.4 (8)
C11–B–C41	115.0 (7)	C24–C25–C26	119.8 (6)
C21–B–C31	110.0 (8)	B–C31–C36	124.4 (6)
C21–B–C41	107.6 (5)	B–C31–C32	121.5 (7)
C31–B–C41	113.3 (4)	C36–C31–C32	114.0 (5)
C11–C12–C13	119.8 (5)	C36–C35–C34	122.2 (9)
B–C11–C12	118.0 (6)	C31–C36–C35	122.3 (8)
B–C11–C16	126.5 (6)	C31–C32–C33	122.7 (8)
C12–C11–C16	115.5 (8)	C35–C34–C33	118.6 (6)
C12–C13–C14	120.4 (8)	C32–C33–C34	120.1 (6)
C11–C16–C15	122.6 (10)	B–C41–C46	119.0 (5)
C13–C14–C15	121.5 (12)	B–C41–C42	124.8 (6)
C16–C15–C14	120.2 (8)	C46–C41–C42	116.1 (8)
C23–C22–C21	125.1 (6)	C41–C46–C45	119.4 (5)
C22–C23–C24	119.8 (6)	C41–C42–C43	122.5 (9)
B–C21–C22	122.9 (8)	C46–C45–C44	123.4 (9)
B–C21–C26	123.4 (7)	C42–C43–C44	121.5 (8)
C22–C21–C26	113.1 (5)	C45–C44–C43	117.1 (9)

Di Vaira, *et al.*,[21] pointed out that by using a two-term potential energy expression of the form $U_{ij} = a_{ij} \exp(-b_{ij}r_{ij}) - c_{ij}r_{ij}^{-6}$ (r_{ij} is the distance in angstroms between atoms i and j and a, b, and c are constants) to calculate the inter-ring interaction energy it is possible to predict the most stable conformation of the tetraphenylborate ion. Moreover, a particular BPh_4^- conformation resulting from a certain structural analysis can be located with respect to the energy minimum and thus its relative conformational stability can be deduced.

Di Vaira, *et al.*,[21] investigated $^1/_2\Sigma_{i\neq j}U_{ij}$ as a function of rotation of the phenyl groups about the B-C bond (including in their calculation only those atoms not on the axis of rotation) and obtained a minimum energy as a function of the four angles ϕ_1, ϕ_2, ϕ_3, and ϕ_4 (defined in ref 21). They also showed that, for the crystallographically determined structures of the BPh_4^- anion in four different systems, each lies at higher energy than the predicted minimum (from 0.8 to 1.8 kcal/mol). We have calculated the conformational energy of the BPh_4^- anion in our system. It was felt that this may cast some light on how readily the BPh_4^- anion packs into this particular crystal system and thus tend to indicate the intrinsic stability of the $[Ni_2(tren)_2(OCN)_2]^{2+}$ cation. If the BPh_4^- anion were judged to be undistorted, energetic stabilization of this arrangement may contribute significantly to the driving force for precipitating a nickel dimer bridged in the fashion we have found.

We have calculated $^1/_2\Sigma_{i\neq j}U_{ij}$ for the BPh_4^- anion configuration in our system (from the parameters in Table V) as well as for the configuration reported by Di Vaira, *et al.*[21]

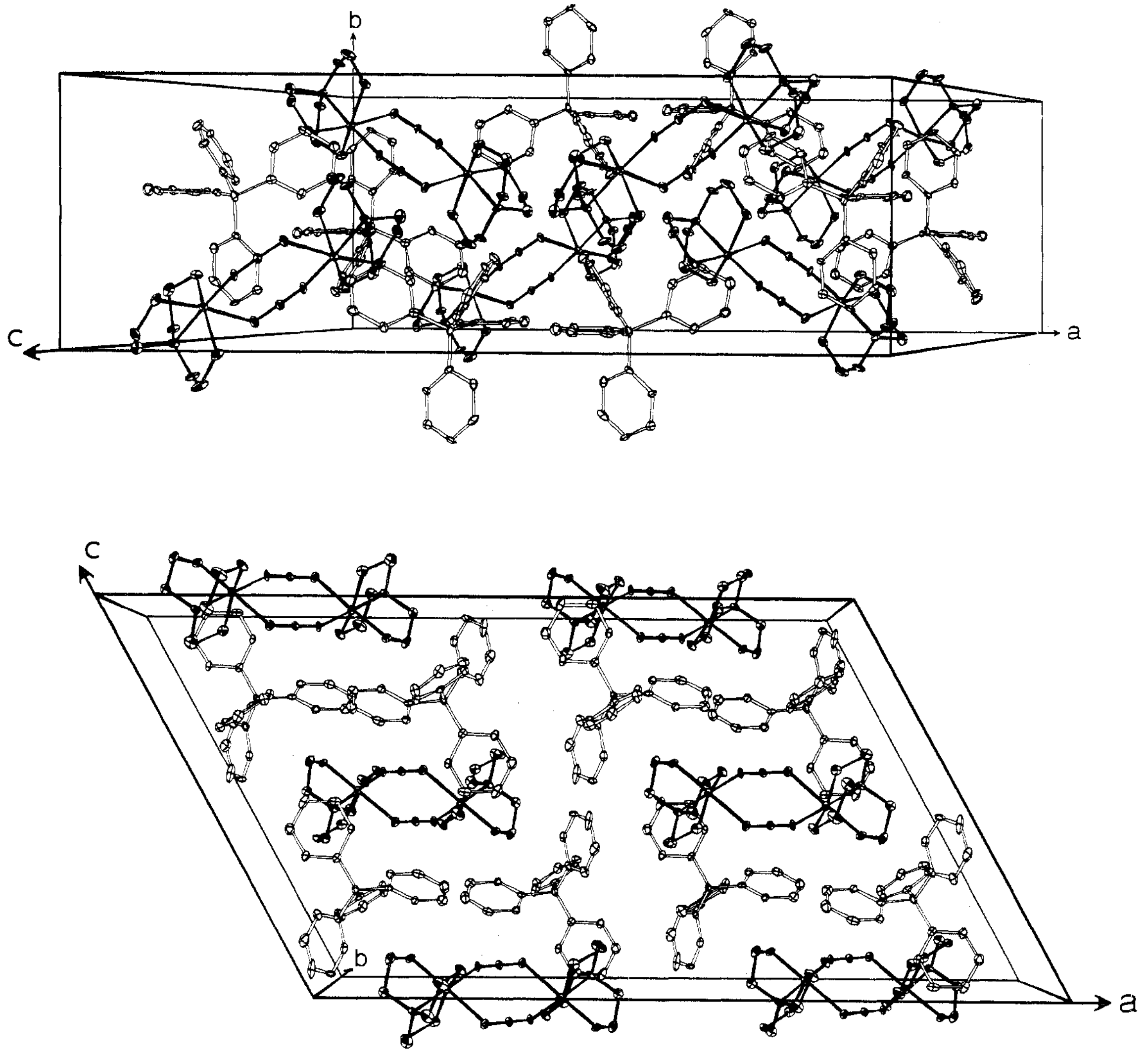

Figure 3. Two perspectives of the crystal packing present in $[Ni_2(tren)_2(OCN)_2](BPh_4)_2$. Hydrogen atoms are not shown.

These computations were performed both including and excluding the phenyl carbon bonded to boron (where the only other atoms considered are those *off* the phenyl group axis, as per ref 21). We found that when the "tertiary" carbon is excluded, the BPh_4^- anion in our system is 0.09 kcal/mol *less* stable than that of Di Vaira (which according to the calculations reported in ref 21 is the least stable of the four systems studied). However, when the tertiary carbon is included, our BPh_4^- anion is *more* stable than that of Di Vaira by 2 kcal/mol. This apparent contradiction can be resolved by a consideration of the details of the structures involved. In Table VII are given the bonding distances and angles for our BPh_4^- anion. Ideally the conformational energy of this anion is dependent *only* on the relative rotational positions of the four phenyl rings (this was an assumption made by Di Vaira, *et al.*[21]). Least-squares planes have been evaluated for our BPh_4^- anion and are given in Table VIII. Examination of Table VIII shows that the boron atom in our structure is on the average 0.12 Å out of the plane of the rings (this is more than 10 standard deviations). The fact that in Di Vaira's structure the boron-ring displacement is 0.05 Å suggests that the largest conformational energy difference between the two structures is due to a breakdown in the assumption that the rotation axis of the rings (taken to be the B-C bond vector) is coplanar with the rings. To search out the most stable tetraphenylborate configuration where the boron-ring plane distances vary as well as the rotational positions would be an inordinately time-consuming task;

Table VIII. Least-Squares Planes for the Phenyl Rings of the Anion $B(C_6H_5)_4^-$, with Deviations and Estimated Errors in Angstroms, the Equation of the Planes Being $Ax + By + Cz - D = 0$

Plane 1: $A = -0.8433, B = 0.5359, C = -0.04191, D = -9.475$

Atom	C11	C12	C13	C14	C15	C16	B
Dist	−0.008	0.007	0.002	−0.019	0.011	0.003	−0.096
Error	0.009	0.010	0.010	0.014	0.013	0.010	0.011

Plane 2: $A = -0.02875, B = 0.9992, C = -0.02808, D = 9.181$

Atom	C21	C22	C23	C24	C25	C26	B
Dist	−0.006	0.010	−0.007	−0.005	0.006	−0.001	0.192
Error	0.007	0.007	0.009	0.008	0.007	0.007	0.010

Plane 3: $A = -0.1978, B = -0.4682, C = -0.8612, D = -11.979$

Atom	C31	C32	C33	C34	C35	C36	B
Dist	0.001	−0.009	0.014	−0.011	−0.001	0.004	0.109
Error	0.007	0.008	0.008	0.010	0.008	0.007	0.009

Plane 4: $A = 0.5306, B = -0.1512, C = -0.8340, D = 4.224$

Atom	C41	C42	C43	C44	C45	C46	B
Dist	0.002	−0.001	0.002	−0.005	0.005	−0.003	−0.065
Error	0.008	0.008	0.009	0.010	0.009	0.008	0.010

Dihedral Angles

Ring A	Ring B	∠AB, deg	Ring A	Ring B	∠AB, deg
1	2	55.9	2	3	64.0
1	3	87.2	2	4	81.8
1	4	60.4	3	4	46.8

however, we suggest that when all atoms are included in an interaction energy calculation, relative conformational energies may be realistically assigned. This treatment tends to indicate that for our system the borate configuration is relatively stable in its packing arrangement with the $[Ni_2(tren)_2(OCN)_2]^{2+}$ dimer, and this indeed may contribute to the driving force enabling us to isolate this compound.

The packing diagrams (see Figure 3) illustrate the facile dimer-tetraphenylborate packing. Two rings of each anion (those roughly perpendicular to the *b* and *c* unit cell axes) effectively isolate chains of dimer molecules in two directions. That these rings include an angle (see Table VIII) of 87.2° which is considerably different from the expected average ring-ring dihedral angle (~70° in ref 21) again points out the considerable conformational mobility of this anion.

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Registry No. $[Ni_2(tren)_2(OCN)_2](BPh_4)_2$, 49660-74-4.

Supplementary Material Available. The final values of $|F_o|$ and $|F_c|$ for 2773 reflections will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2056.

Contribution from the Division of Natural Sciences and Mathematics, University of Regina, Regina, Saskatchewan, Canada, and the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

Nitrosodisulfonates and Hydroxylamine-*N,N*-disulfonates. II. Crystal Structure of a Rubidium Hydroxylamine-*N,N*-disulfonate

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The crystal structure of $Rb_5\{[ON(SO_3)_2]_2H\}\cdot 3H_2O$ has been determined by direct methods and refined by the full-matrix least-squares method to a weighted residue of 0.071, using 3256 independent reflections measured by diffractometer. The crystals are triclinic: $a = 9.357\ (6)$ Å, $b = 11.109\ (7)$ Å, $c = 11.206\ (5)$ Å, $\alpha = 102.03\ (3)°$, $\beta = 99.09\ (4)°$, $\gamma = 115.53\ (4)°$. The structure contains 2 formula units in the space group $P\bar{1}$, and the two $\{[ON(SO_3)_2]_2H\}^{5-}$ anions occupy each of two independent centers of symmetry. The two $[ON(SO_3)_2]^{3-}$ groups in each anion are joined by a symmetric hydrogen bond; the O–H–O distances are 2.41 (2) and 2.43 (2) Å. The $\{[ON(SO_3)_2]_2H\}^{5-}$ anions are separated by the Rb^+ cations and water molecules.

A future article[1] discusses the preparation, characterization, and magnetic susceptibility of a series of hydroxylamine-*N,N*-disulfonates. A number of crystalline modifications of rubidium hydroxylamine-*N,N*-disulfonate have been prepared and identified. One has been characterized by an X-ray diffraction study and is reported here.

Experimental Section

Crystals of modification II[1] of rubidium hydroxylamine-*N,N*-disulfonate $\{[HON(SO_3)_2]^{2-}\cdot 2Rb^+\cdot {}^1/_2 RbOH\cdot H_2O\}$ were larger than required for crystallographic studies and it was therefore necessary to fracture them. The fracture surfaces were curved. An attempt was made to grind the crystals to spheres but they shattered immediately in the sphere grinder. A sample of approximate dimensions 0.03 cm with irregular shape was finally selected for data collection. The approximate lattice constants and orientation of the crystal were first determined by film methods. The Laue symmetry indicated a triclinic space group.

The crystal was placed on a Picker FACS-I automated diffractometer equipped with a highly oriented graphite monochromator. The lattice constants were determined by a least-squares fit to the positions of 12 reflections with 2θ values between 39 and 42° as observed using Mo $K\alpha_1$ radiation. The lattice constants determined in this way were $a = 9.357\ (6)$ Å, $b = 11.109\ (7)$ Å, $c = 11.206\ (5)$ Å, $\alpha = 102.03\ (3)°$, $\beta = 99.09\ (4)°$, $\gamma = 115.53\ (4)°$, and $V = 986.6$ Å^3, at 20°. Assuming 4 formula units per unit cell and a formula weight of 432.1, based on the stoichiometry given above, the calculated density is 2.93 g cm^{-3} which compares with a measured value of 2.85 g cm^{-3} obtained by picnometry. The linear absorption coefficient for Mo $K\alpha$ radiation is 50.1 cm^{-1}. The integrated intensities of 4574 independent reflections were measured using the θ-2θ scan mode and Mo $K\alpha$ radiation. Data were collected between 0 and 38° in 2θ with a scan rate of 2° min^{-1} and 10-sec background counts on each side of the peak. Data were also collected between 38 and 55° in 2θ with a 1° min^{-1} scan rate and 40-sec background counts. The intensities of three standard reflections were checked after each set of 98 data points was collected. These reflections decreased in intensity by roughly 30% over the time of the data collection. The average fluctuations between the intensities of successive standard reflections were of the order of magnitude expected from counting statistical errors. The data were corrected for the decrease in intensity using the averaged intensities of the three standards at each point at which standards were collected and interpolating linearly between each successive set of standards.

The data were then reduced to observed structure factors by standard methods. The polarization factor used was $(\cos^2 2\theta_m + \cos^2 2\theta_s)/2 \sin \theta_s$ where θ_m and θ_s are the monochromator and sample Bragg angles, respectively. The scattering factors were calculated from the series coefficients given by Cromer and Mann.[2]

Normalized structure factors were calculated, and from the average values of $|E|$ and $|E^2 - 1|$ (0.793 and 0.926) the space group was inferred to be $P\bar{1}$. The 396 reflections with $|E| > 1.71$ were used with the logical symbolic addition method (LSAM) programs of Germain and Woolfson.[3] None of the E maps generated using these programs were chemically reasonable. The convergence elimination algorithm, which is part of the MULTAN direct-methods

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[1] B. D. Perlson, D. B. Russell, and B. E. Robertson, *Inorg. Chem.*, in press.

[2] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

[3] G. Germain and M. M. Woolfson, *Acta Crystallogr., Sect. B*, 24, 91 (1968).